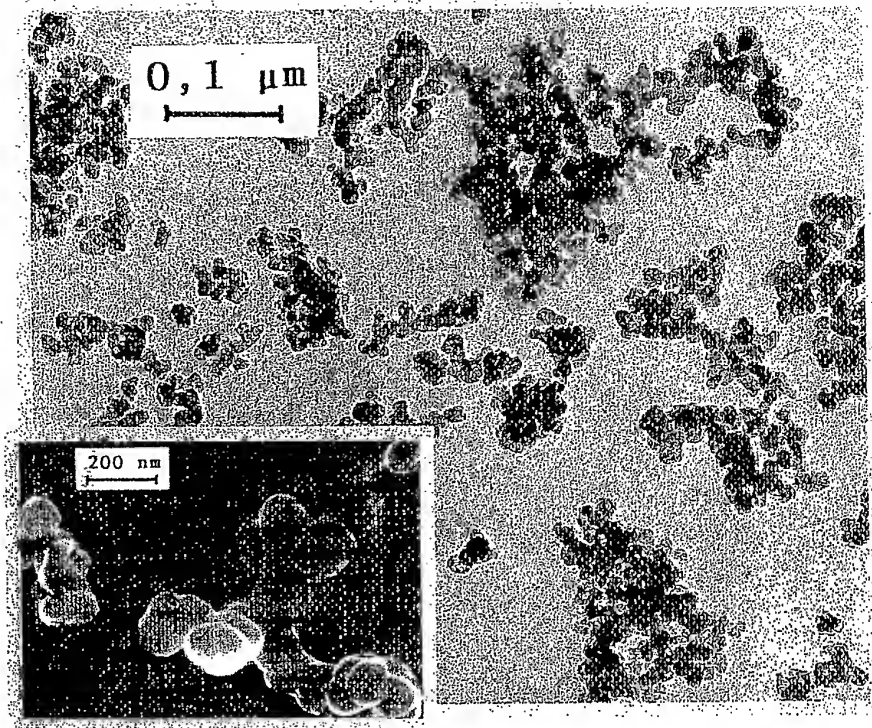


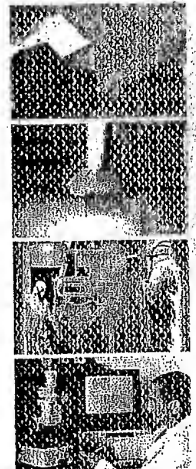
Exhibit 1

Die Technologie des Beschichtens – Pigmentrusse



Horst Ferch

Pigmentruße



VINCENTZ

Herausgegeben von Ulrich Zorll

Umschlagbilder: ECI, Buss, Sun Chemical, Jungheinrich AG, (Warmbold)
Ferch

Die Technologie des Beschichtens

Dr. Horst Ferch

Pigmentruße

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Herausgegeben von Dr. Ulrich Zorll

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27

2 Herstellungsverfahren und Nachbehandlung

In Tabelle 9 wiedergegeben ist ein Überblick über die Herstellungsverfahren für Industrieruße. Ausführlich werden weiterhin nur die Verfahren der thermisch-oxidativen Spaltung behandelt. Da die Industrieruße, erzeugt nach thermischen Verfahren, keine nennenswerte Anwendung als Pigmentruße haben, werden diese und andere technisch gewonnene Produkte nur kurz beschrieben.

Chemischer Prozeß	Herstellungsverfahren (angewendet seit:)	Rohstoffe	Anzahl der Flammen	Besonderheit
Thermisch-oxidative Spaltung	Furnace-Verfahren (1922)	Erdöl, Erdgas oder Öle auf Steinkohlenbasis	1 pro Anlage	geregelte und steuerbare Luftzufuhr
	Degussa-Gasruß-Verfahren (1935)	Steinkohlen-teer-Destillate	zahlreiche	Luftzufuhr nur in engen Grenzen regelbar
	Flammruß-Verfahren (ca. 100 v. Chr.)	Aromatische Öle auf Basis von Kohle oder Öl	1 pro Anlage	wie bei Gasruß, nur grobteilige Ruße herstellbar
Thermische Spaltung	Thermalruß-Verfahren (ca. 1935)	vorwiegend Erdgas	keine	nur grobteilige Ruße herstellbar
	Acetylenruß-Verfahren (1905)	Acetylen	keine	hohes Saugvermögen der Ruße

Tabelle 9: Herstellungsverfahren von Industrierußen

Ergänzend sei vermerkt, daß das Channel-Verfahren, mit Erdgas betrieben und bis 1974 in den USA genutzt, jetzt nur historische Bedeutung hat; es entsprach dem Degussa-Gasrußverfahren.

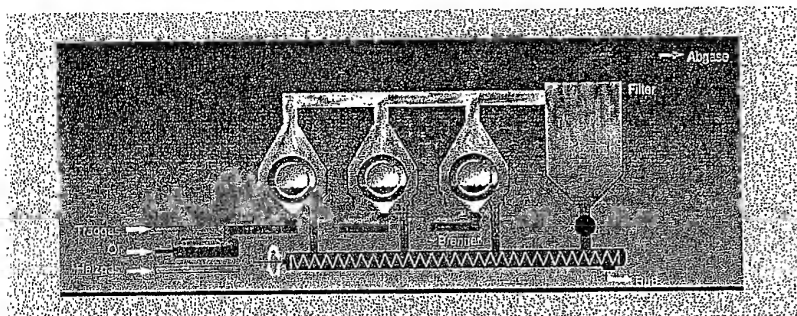


Abbildung 4: Schematische Darstellung des Degussa-Gasrußverfahrens

Im Gegensatz zum Furnace-Verfahren arbeitet man beim Gasruß-Verfahren *nicht* in einem völlig geschlossenen System. Da immer Luftüberschuß besteht, haben *Gasruße im Vergleich zu Furnace-Rußen viel mehr sauerstofffunktionelle Oberflächengruppen*. In wäßriger Aufschlämmung reagieren Gasruße – anders als Furnace-Ruße – sauer.

Im Vergleich zum Channel- ist das Degussa-Gasruß-Verfahren umweltschonender. Variabilität gibt es zudem in der Rohstoffauswahl und bei der Einstellung der Primärteilchengröße; sie liegt für Gasruße im Bereich von 10 bis 30 nm. Die Rußstruktur ist nicht zu beeinflussen.

Gasruße zeichnen sich durch gute Benetzbarkeit aus, was die Dispergierbarkeit deutlich verbessert. Höher ist zudem im Vergleich zu Furnacerußen die Stabilität von Gasruß-Anreibungen. Einsatz finden deshalb Gasruße heute praktisch nur im Pigmentbereich, nachdem sie ihre frühere Bedeutung als Laufflächenruße in der Gummi-Industrie fast völlig verloren haben. Als sich absehen ließ, daß die Channel-Ruß-Produktion in den USA eingestellt würde, kam 1966 ein „DCR“-Ruß (Degussa channel replacement) auf den Markt.

Kenndaten für Gasruße enthält Tabelle 10; eine hochauflösende TEM-Aufnahme eines typischen Gasrußes ist in Abbildung 5 gezeigt, deren Vergrößerung übrigens im Vergleich zur analogen Abbildung 3 etwa doppelt so groß ist.

2.3 Flammruß-Verfahren

Das Erzeugen von Flammruß (lamp black) gehört zu den ältesten Ruß-Herstellungsprozessen. Auch in deutschen Patenten zur Herstellung des heute Flammruß genannten Produkts findet sich die ältere Bezeichnung „Lampenruße“

3 Chemische Eigenschaften

3.1 Zusammensetzung

Wie schon eingangs ausgeführt, stellen Industrieruße eine stark gestörte Erscheinungsform des graphitischen Kohlenstoffs dar. Die chemische Bezeichnung C für Kohlenstoff ist bei Industrierußen ohne weitere Aussage und daher ungebräuchlich. Industrieruße, die aus Flammenprozessen stammen (→ Tabelle 9), erhalten teilweise etwa 1 % Wasserstoff, so daß früher die empirische Formel C_8H ins Spiel gebracht wurde. Doch diese Formel hat ebenfalls keine Aussagekraft [47].

Neben Kohlenstoff und Wasserstoff läßt die Elementaranalyse von Industrieruß noch eine Reihe anderer Elemente erkennen. *Tabelle 14* zeigt die Zusammensetzung einiger Industrieruß-Gruppen bzw. die von typischen Einzelrußen. Die meisten dieser Elemente sind an der Oberfläche konzentriert; Stickstoff und Schwefel sind zum Teil im Rußteilchen eingebaut [130], da ihre Anwesenheit rohstoffbedingt ist.

	C	H	O	N	S	Ver- aschungs- rückstand
Grenzen von Industrierußen	83 bis 99,5	0,2 bis 1	0,2 bis 15	0 bis 0,7	0,1 bis 1,5	0,05 bis 1,3
Furnaceruße	97,3 bis 98	0,3 bis 0,6	0,5 bis 1	0,2 bis 0,3	0,2 bis 0,5	0,1 bis 1,3
dgl. oxidiert	96,5 bis 97	0,4 bis 0,6	1 bis 2	0,2 bis 0,3	0,2 bis 0,5	0,1 bis 0,5
grobteilige Gasruße	96,5	1	2	0,1	0,2 bis 0,4	0,04
feinteilige Gasruße	94,5 bis 96	1	2,5 bis 4	0,1 bis 0,2	0,2 bis 0,3	0,01 bis 0,04
dgl. oxidiert	83 bis 89	1	9 bis 15	0,5 bis 0,7	0,2 bis 0,3	0,02 bis 0,04
Flammruß 101	98,5	0,4	0,4	0,1	0,3 bis 0,7	0,05 bis 0,2
„Printex XE 2“	—	—	—	0,4	0,4	1

Tabelle 14: Chemische Zusammensetzungen und Veraschungsrückstände von Industrierußen (in Prozent)

Bei Industrierußen besteht anscheinend eine „aromatische Natur“ [131]. Mit Lösemitteln kann man geringe Mengen an organischen Bestandteilen von der Oberfläche der Industrieruße ablösen. Früher trug der Wert, den man bei solch nicht genau festgelegten Tests erhielt, die Bezeichnung „Empyreuma“. Im Industriezeitalter wird statt dessen der Toluolextrakt bestimmt. (→ 3.5). Man findet hierfür bei den Industrierußen weniger als 0,35 %, oft sogar Werte unter 0,1 %.

Analysiert man das extrahierte Material, so findet man unter anderem geringe Mengen an polyaromatischen oder polycyclischen Kohlenwasserstoffen (= polyaromatic hydrocarbons; oft PAHs abgekürzt). Das Element Wasserstoff der

Die Reproduzierbarkeit der titrimetrischen Bestimmung funktioneller Gruppen mit Basen ist erfahrungsgemäß gut. Eine Vorstellung von den an der Industrieruß-Oberfläche nachgewiesenen sauerstoffhaltigen funktionellen Gruppen vermittelt die Abbildung 8.

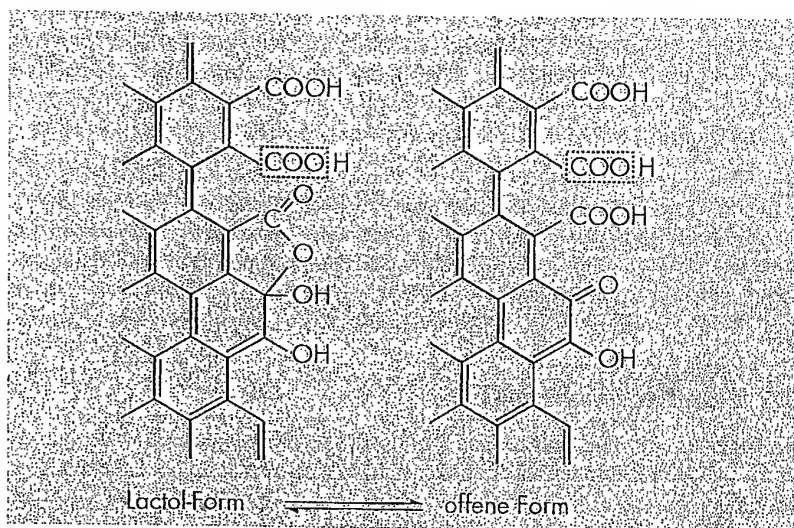


Abbildung 8: Funktionelle sauerstoffhaltige Gruppen an der Oberfläche von Industrieruß

Neben sauren Oberflächenoxiden gibt es auch basisch reagierende Gruppen [137, 138], deren Existenz seit langem bekannt ist [139]. Die basischen Oberflächengruppen werden durch Neutralisation mit N/20 Salz- oder Schwefelsäure bestimmt. Die Pyronstruktur läßt sich zur partiellen Erklärung des basischen pH-Wertes nicht oxidativ nachbehandelter Furnaceruße heranziehen (Abbildung 9) [43].

Die sauerstofffunktionellen Gruppen sind chemisch relativ fest an der Oberfläche der Industrieruße gebunden. Durch Erhitzen auf 950°C werden sie zusammen mit den PAHs (→ 3.1) weitgehend verflüchtigt. Daruf beruht die Bestimmung der „flüchtigen Bestandteile“.

Es fällt übrigens auf, daß Furnaceruße praktisch keine Carboxylgruppen aufweisen, auch Lactongruppierungen sind an ihnen nur gering vertreten. Dafür tragen *Furnaceruße basische Oxide, die bei allen Gasrußen fehlen.* Mit

- Bezeichnung „pyrolytic volatile analysis“ auf. Hiernach werden freigesetzt
- Kohlendioxid bis etwa 800 °C, wobei bis 300 °C Carboxylatanionen, zwischen 400 und 500 °C nichtionisierte Carboxylgruppen zersetzt werden [421],
 - Kohlenmonoxid im Bereich zwischen 350 und 1050 °C,
 - Wasserstoff bei Temperaturen zwischen 650 und 1500 °C.

Durch polarografische Messungen wurde die Existenz von chinon- bzw. hydrochinonartigen Gruppen auf der Oberfläche von Industrieruß nachgewiesen [435]. Auf potentiometrischem Wege war es möglich, die Konzentration von =CO- und ≡CH-Gruppen [436] sowie jene der oberflächenaktiven Gruppen in der Größenordnung von 10^{-10} bis 10^{-11} Mol/cm² zu bestimmen [437].

3.2.2 Weitere Erkenntnisse

Wasserstoff ist an der Oberfläche von Industrieruß in Form von CH-Gruppen gebunden, und zwar an den Ecken der Kohlenstoffschichten. Daneben gibt es den „aktiven Wasserstoff“ an den funktionellen Gruppen. Er läßt sich nach dem Entgasen mit LiAlH₄ bei 70 °C bestimmen. Die Hydrierung der Oberfläche von Industrieruß erfolgt mit diesem Reagenz über längere Zeiten bei 125 °C [43].

Doppelbindungen an der Oberfläche von Industrieruß lassen sich durch Bromierung [144] oder über die Messung von Benetzungswärmen bestimmen. Beim Bromieren wird 1 g Pigmentruß mit 0,25 ml Brom in 100-ml-Bombenrohr 100 Stunden auf 100 °C erhitzt und anschließend bei dieser Temperatur 1 Stunde bei 10^{-3} mbar entgast. Hohe Bromaufnahme und hohe Benetzungswärme entsprechen sich. Mit hoher Benetzungswärme geht bei Gummirußen auch die flächenspezifisch stärkste Wechselwirkung im Kautschuk einher.

Über Schwefel- und Stickstoffverbindungen an der Oberfläche von Industrierußen ist nichts bekannt.

3.2.3 Bedeutung der Oberflächenchemie für die Praxis

Unter Verwendung aller bekannten Zusammenhänge lassen sich aus den Erkenntnissen zur Oberflächenchemie und deren Anwendung folgende Regeln ableiten [100]:

- bei gleicher Primärteilchengröße und Struktur sollen sauerstoffarme Pigmentruße für unpolare und sauerstoffreiche Pigmente für polare Bindemittel verwendet werden,
- oxidativ nachbehandelte Pigmentruße lassen sich z. B. in Alkydharzen besser und damit unter vergleichbaren Dispergierbedingungen schneller dispergieren als die entsprechenden Ausgangsruße,

- für zahlreiche Bindemittel des Lacksektors ist auch die Verträglichkeit von oxidierten Pigmentrußen besser, so daß eine höhere Stabilität gegenüber Flockulation oder Ausschwimmen besteht,
- auf Grund des geringeren Öl- oder Bindemittelbedarfs lassen sich mit oxidierten Pigmentrußen höhere PVK-Werte in Anreibepasten erreichen, wobei sich dennoch niedrige Verarbeitungsviskositäten ergeben können. Bei der Lagerung steigt zudem die Viskosität nicht so stark an.
- bei vergleichbarer Primärteilchengröße absorbieren sauerstoffreiche Pigmentruße mehr Feuchtigkeit und mehr Schwermetallionen.

Neueren Ursprungs sind Erfahrungen, daß sich oxidierte Gasruße in wäßrigen Medien nicht so gut eignen wie normale Gasruße. Diese Aussage gilt für

- wasserverdünnbare, tiefschwarze Lacksysteme sowie für
- wasserverdünnbare Druckfarben und ink jet-Farben.

In allen Fällen ist die Flockulationstendenz bei der Lagerung mit Gasrußen besser als bei den entsprechenden oxidierten Pigmentrußen. Gasruße verhalten sich auch besser als Furnaceruße oder deren oxidierte Varianten.

3.3 pH-Wert

Die Bestimmung des pH-Wertes von Pigmentrußen erfolgt nach DIN ISO 387/9 (früher nach DIN 53200). Als pH-Wert von Pigmentrußen gilt stets der einer entsprechenden wäßrigen Dispersion. Geperlte Industrieruße müssen vor der Einwaage pulverisiert werden.

Der Sauerstoffgehalt eines Industrierußes ist nicht nur von größter Bedeutung für die Anwendung, sondern er bestimmt nach Form und Konzentration der maßgebenden Oberflächengruppen auch die Höhe des pH-Wertes. Liefert ein Pigmentruß Werte im sauren Bereich, so handelt es sich um einen Gasruß, denn

- unbehandelte Gasruße zeigen pH-Werte um 4,
- oxidierte Gasruße solche zwischen 2 und 4.

Furnaceruße, im reduzierenden Medium hergestellt, haben auf Grund ihrer basischen Gruppen pH-Werte von 7 bis 10. Der pH-Wert von Flammruß liegt bei 7,5.

Im geringen Maße ist der pH-Wert der Furnaceruße auch von der Qualität des Quenchwassers abhängig, da es vor allem Erdalkaliverbindungen in den Industrieruß einträgt. Auch adsorbierte Gase, von Nachbehandlungsmethoden herrührend, können zusätzlich zur chemischen Natur der Oberflächengruppen den pH-Wert beeinflussen. Erwähnt wurde bereits die starke Veränderung des pH-Wertes von Pigmentrußen durch eine oxidative Nachbehandlung.

Exhibit 2

Translation of Portions of German Language Publication

**TRANSLATION OF PORTIONS OF
GERMAN LANGUAGE PUBLICATION**

(A)

Chemical process	Production process (employed since:)	Raw material	Number of flames	Special features
Thermal oxidative cleavage	Furnace process (1922)	Crude petroleum, natural gas, or oils based on hard coal	1 per plant	Regulated and controllable supply of air
	Degussa gas black process (1935)	Hard coal tar distillates	Numerous	Supply of air controllable only within narrow limits
	Flame soot process (ca. 100 B.C.E.)	Aromatic oils based on coal or oil	1 per plant	Like gas soot; only coarse-grained soots can be produced
Thermal cleavage	Thermal soot process (ca. 1935)	Primarily natural gas	None	Only coarse-grained soots can be produced
	Acetylene soot process (1905)	Acetylene	None	High pumping capacity of the soots

Table 9: Production of industrial soots

(B)

In addition, it is noted that the channel process, operated with natural gas and utilized in the USA up to 1974, is now of historical importance only; it corresponded to the Degussa gas black process.

(C)

In contrast to the furnace process, work in the gas black process is *not* carried out in a completely closed system. Because an excess of air is always present, *gas soots, in comparison to furnace soots, have many more oxygen-functional surface groups*. In aqueous slurry, gas soots react in an acidic manner – in contrast to furnace soots.

In comparison to the channel process, the Degussa gas black process is more protective of the environment. In addition, there exists variability in the choice of raw materials and in the adjustment of the primary particle size, which lies in the range of 10 to 30 nm for gas soots. The soot structure cannot be influenced.

Gas soots are characterized by good wettability, which markedly improves their dispersion capability. In addition, in comparison to furnace soots, the stability of gas soot grindings is higher. Therefore, gas soots find application nowadays practically only in the area of pigments, after having nearly completely lost their earlier importance as tread soots in the rubber industry. Once it became evident that the production of channel soot in the USA would end, a “DCR” (Degussa channel replacement) soot came on the market in 1966.

(D)

	C	H	O	N	S	Ashing residue
Limits of industrial soots	83 to 99.5	0.2 to 1	0.2 to 15	0 to 0.7	0.1 to 1.5	0.03 to 1.3
Furnace soots	97.3 to 98	0.3 to 0.6	0.5 to 1	0.2 to 0.3	0.2 to 0.5	0.1 to 0.3
The same, oxidized	96.5 to 97	0.4 to 0.6	1 to 2	0.2 to 0.3	0.2 to 0.5	0.1 to 0.5
Coarse-grained gas soots	96.5	1	2	0.1	0.2 to 0.4	0.04
Fine-grained gas soots	94.5 to 96	1	2.5 to 4	0.1 to 0.2	0.2 to 0.3	0.01 to 0.04
The same, oxidized	83 to 89	1	9 to 15	0.5 to 0.7	0.2 to 0.3	0.02 to 0.04
Flame soot 101	98.5	0.4	0.4	0.1	0.3 to 0.7	0.05 to 0.2
“Printex XE 2”		-	-	0.4	0.4	1

Table 14: Chemical compositions and ashing residues of industrial soots (in percent)

(E)

Moreover, it is noticeable that furnace soots have practically no carboxyl groups; even lactone groups are present in them to only a slight extent. On the other hand, *furnace soots bear basic oxides, which are absent in all gas soots.*

(F)

3.2.3 The Importance of Surface Chemistry in Practice

Using all known interrelationships, it is possible from what is known in regard to surface chemistry and the application thereof to deduce the following rules [100]:

- Given the same primary particle sizes and structure, oxygen-poor pigment soots should be used for nonpolar and oxygen-rich pigments for polar binders;
- Oxidatively after-treated pigment soots can be dispersed better in, for example, alkyd resins and accordingly, under comparable dispersing conditions, more rapidly than the corresponding starting soots;

(G)

Of more recent origin is the finding that oxidized gas soots are not as suitable in aqueous media as normal gas soots. This assertion holds for

- water-dilutable, deep-black lacquer systems as well as for water-dilutable printing inks and ink jet inks.

In all cases, the flocculating tendency is better during the storage with gas soots than for the corresponding oxidized pigment soots. Gas soots also exhibit better behavior than furnace soots or the oxidized variants thereof.

Exhibit 3

Ullmann's Encyclopedia of Industrial Chemistry

ULLMANN'S

Standort: BIBL. WOLFGANG

Ullmann's Encyclopedia of Industrial Chemistry



Sixth, Completely Revised Edition

Volume 6

Butenes
to
Cellulose Ethers

 WILEY-VCH

Wissenschaftliche Bibliothek Wolfgang



BW05-0126

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45 % of production is powdered activated carbon and about 55 % is granular and extruded activated carbon (pellets). The largest producers, divided by country, are given in the following:

America USA	Anticarb Burnbey and Sutcliffe Corp. Calgon Carbon Corp. Norit American Inc. Westvaco Corp.
Brasil Mexico	Industria Quimica Carbonifera Chrimex SA de CV Nobrac Mexicana SA de CV
Europe Belgium France	Chemviron Carbon Ceon Pica
Germany	A.U.G. CarboTech Aktivkohlen GmbH
Netherlands UK Asia China	Norit Norit UK Oatong Yungghun Activated Carbon Plant Ningxia Hualun Activated Carbon Co. Ningxia Longde Activated Carbon plant Shansi Derong Minerals Bureau Huni Yu Shan Activated Carbon Group Tianjin Anfull Chemical Co. Ltd. Zhejiang Shuehang Activated Carbon Co. Indian Dyestuff Industries Indo German Carbon Ltd.
India	PT. Ikaindo
Indonesia Japan	Futamura Chemical Industries Kuramy Chemicals Mitsubishi Chemicals Sankyo Sangyo Takeda Chemical Industries
Malaysia	Century Chemical Works
Philippines	Pacific Activated Carbon Cempro Chemical Divao Central Chemical Philippine Activated Carbon Philippines Japan Activated Carbon Bieco-Link Carbon
Sri Lanka	Haycarb Tijit
Taiwan	China Activated Carbon Industries Taiwan Active Carbon Industries Carbokarn Thailand

6. Carbon Black

Carbon black [1333-86-4] and soot are formed either by pyrolysis or by partial combustion of vapors containing carbon. Soot as an unwanted byproduct of combustion (e.g., in chimneys or diesel engines) is a poorly defined material. Besides carbon black particles, it often contains significant amounts of ash and large amounts of polycyclic aromatic hydrocarbons (PAH) [413]. Residual hydrocarbons, which can

be determined by extraction with solvents (e.g., toluene), can account for 30 wt %.

On the other hand, the term "carbon black" is used for a group of well-defined, industrial manufactured products, which are produced under carefully controlled conditions. The physical and chemical properties of each grade of carbon black are kept within narrow specification. Carbon black is one form of highly dispersed elemental carbon with extremely small particles. Depending on the production process and the raw materials, carbon black also contains chemically bound hydrogen, oxygen, nitrogen, and sulfur.

Due to its excellent pigmentation properties, especially its light stability and universal insolubility, carbon black has been used as a black pigment since early times. It was produced for this purpose by burning oils, fats, or resinous materials. The flame was either quenched on a cool surface (impingement black) or cooled in special chimneys (lamp black), where the carbon black was deposited.

Both processes are still used for the production of carbon black. The channel black process, a process for making impingement blacks, has been used in the United States since the end of the 19th century. This process, which has now been abandoned because of economic and environmental considerations, used natural gas as raw material. A similar process for the production of impingement blacks, the "Degussa gas black process," is still used today.

The increasing demand for carbon black led to new production processes. The most important process today is the furnace black process. It was developed in the United States in the 1930s and substantially improved after World War II. It is a continuous process, which allows the production of a variety of carbon black grades under carefully controlled conditions. Nearly all rubber grades and a significant part of pigment-grade carbon blacks are now manufactured by the furnace black process. Nevertheless, other processes, such as gas black, lamp black, thermal black, and acetylene black processes, are still used for the production of specialties.

While carbon black was exclusively used as a pigment until the beginning of this century, its use as an active filler in rubber was the starting point for a new rapidly expanding application. In the production of automobile tires, it was

found that treads filled with carbon black had a markedly higher abrasion resistance than those filled with zinc oxide. This discovery, together with increasing use of motor vehicles, was the basis for the present importance of carbon black as a filler in rubber.

Today at least 35 different grades of carbon black are used as fillers in rubber, and about 80 are used in pigments or special applications. The total world production in 1994 was 6×10^6 t, of which ca. 90 % was used in the rubber industry.

6.1. Physical Properties

Morphology. Electron micrographs show that the primary particles of carbon black are almost spherical. In general, a larger number of such primary particles builds aggregates in the form of chains or clusters. In practice, the degree of aggregation is called the "structure" of carbon black. These aggregates tend to agglomerate.

The mean primary particle diameter, the width of the particle size distribution, and the degree of aggregation can be varied within relatively wide ranges (Figs. 52, 53, 54) by varying the production process and several process parameters.

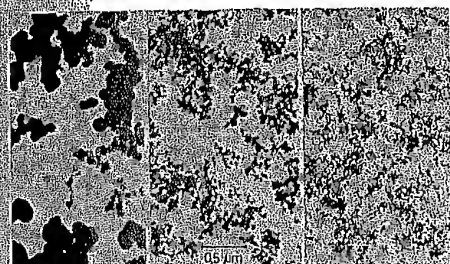


Figure 52. Carbon blacks of different primary particle sizes and specific surface areas

From left to right: lamp black (mean primary particle diameter, 95 nm, BET surface area $21 \text{ m}^2/\text{g}$), furnace black (27 nm, $90 \text{ m}^2/\text{g}$), finely divided gas black (13 nm, $320 \text{ m}^2/\text{g}$)

The diameter of the primary particles ranges from 5 to 500 nm. Diffraction patterns produced by the so-called phase-contrast method in high-resolution electron microscopy show that the spherical primary particles are not amorphous (Fig. 55). They consist of relatively disordered nuclei surrounded by concentrically deposited carbon layers [414]. The degree of order increases from the center to the periphery of each

particle, a phenomenon important to the understanding of the chemical reactivity of carbon black.

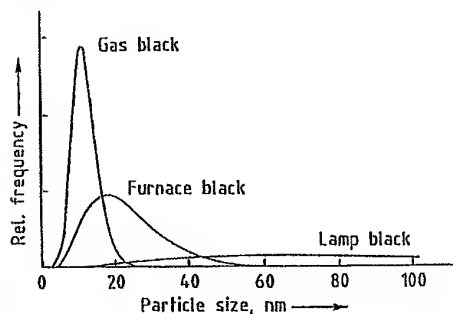


Figure 53. Particle distribution curves for the carbon blacks of Figure 52

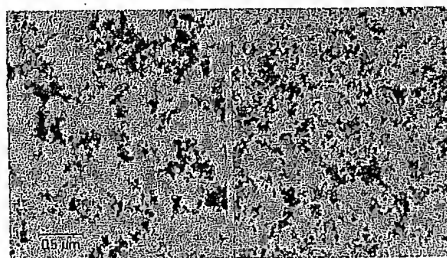


Figure 54. Furnace blacks of different aggregation degrees

The carbon atoms within each layer are arranged in almost the same manner as in graphite. The layers are almost parallel to each other; however, the relative position of these layers is random, so that there is no order as in the *c* direction of graphite ("turbostratic structure") [415]. X-ray diffraction permits the determination of "crystalline" regions within the carbon black primary particle. These regions are parts of more extended layers, not isolated crystallites. X-ray diffraction reflexes are observed wherever parts of at least three layers are parallel and equidistant. For most carbon blacks, these "crystalline" regions are 1.5–2.0 nm in length and 1.2–1.5 nm in height, corresponding to 4–5 carbon layers [416]. The fraction of "crystalline" or well-ordered carbon in carbon blacks varies according to oxidation kinetic studies between 60 and 90 %.

The morphology of carbon black primary particles indicates that during formation of carbon black, the first nuclei of pyrolyzed hydrocarbons condensate from the gas phase. Thereafter,

further carbon layers or their precursors are adsorbed onto the surface of the growing particle. Due to this adsorption, the new layers are always orientated parallel to the existing surface. In the case of high-structure carbon blacks, several particles are joined by collision while they grow. Aggregates are formed by further carbon deposits on these initially loose agglomerates. Polyacetylene seems to play a role in the formation of precursors when aliphatic hydrocarbons are used as starting materials. With aromatic raw materials, however, it is more likely that aromatic degradation products are the intermediates.

The carbon layers of carbon black rearrange to a graphitic order, beginning at the particle surface at temperatures above 1200 °C. At 3000 °C, graphite crystallites are formed and the carbon black particles assume polyhedral shape.

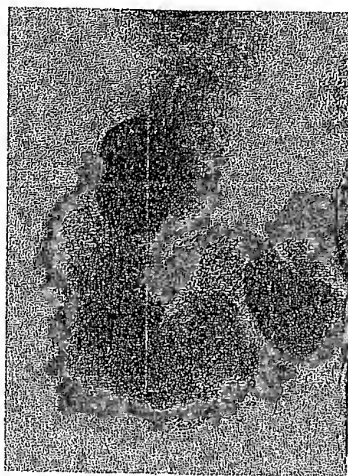


Figure 55. Phase-contrast electron micrograph of a carbon black aggregate

Specific Surface Area. The specific surface area of industrial carbon blacks varies widely. While coarse thermal blacks have specific surface areas as small as 8 m²/g, the finest pigment grades can have specific surface areas as large as 1000 m²/g. The specific surface areas of carbon blacks used as reinforcing fillers in tire treads lie between 80 and 150 m²/g. In general, carbon blacks with specific surface areas > 150 m²/g are porous with pore diameters of less than 1.0 nm. The area within the pores of

high-surface-area carbon blacks can exceed the outer (geometrical) surface area of the particles

Adsorption Properties. Due to their large specific surface areas, carbon blacks have a remarkable adsorption capacity for water, solvents, binders, and polymers, depending on their surface chemistry. Adsorption capacity increases with increasing specific surface area and porosity. Chemical and physical adsorption not only determine wettability and dispersibility to a great extent, but are also most important factors in the use of carbon blacks as fillers in rubber as well as in their use as pigments. Carbon blacks with high specific surface areas can adsorb up to 20 wt % of water when exposed to humid air. In some cases, the adsorption of stabilizers or accelerators can pose a problem in polymer systems.

Density. Density measurements using the helium displacement method yield values between 1.8 and 2.1 g/cm³ for different grades of carbon black. A mean density value of 1.86 g/cm³ is commonly used for the calculation of electron microscopic surface areas. Graphitization raises the density to 2.18 g/cm³. The lower density with respect to graphite (2.266 g/cm³) is due to slightly greater layer distances.

Electrical Conductivity. The electrical conductivity of carbon blacks is inferior to that of graphite, and is dependent on the type of production process, as well as on the specific surface area and structure. Since the limiting factor in electrical conductivity is generally the transition resistance between neighboring particles, compression or concentration of pure or dispersed carbon black, respectively, plays an important role. Special grades of carbon black are used to give polymers antistatic or electrically conductive properties. Carbon blacks with high conductivity and high adsorption capacity for electrolyte solutions are used in dry-cell batteries.

Light Absorption. The wide use of carbon blacks as black pigments is due to their absorption of visible light. The absorption rate can reach 99.8 %. The black color can take on a bluish or brownish tone, depending on light scattering, wavelength, the type of carbon black, and

the system into which the carbon black is incorporated. Infrared and ultraviolet light is also absorbed. Therefore, some carbon blacks are used as UV stabilizers in plastics.

6.2. Chemical Properties

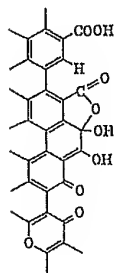
Chemical Composition and Surface Chemistry. The global chemical composition according to elemental analysis is within the following limits:

carbon 80.0–99.5 wt %
hydrogen 0.3–1.3 wt %
oxygen 0.5–15.0 wt %
nitrogen 0.1–0.7 wt %
sulfur 0.1–0.7 wt %

depending on the manufacturing process, raw material, and possible chemical aftertreatment. The ash content of most furnace blacks is < 1 wt %. The ash components can result from the raw material, the salts which are injected to control the structure, and salts in the process water. The ash content of gas blacks is less than 0.02 %.

The surface of carbon blacks contains certain amounts of polynuclear aromatic substances. These are strongly adsorbed and can only be isolated by continuous extraction with solvents, e.g., boiling toluene. For most industrial pigment-grade carbon blacks, the amount of extractable material is below the limit defined by the food laws.

The hydrogen in carbon black is bound as CH groups at the edge of the carbon layers. Nitrogen seems to be primarily integrated into the aromatic layer system as heteroatoms.



The oxygen content of carbon blacks is of great importance for their application. Oxygen

is bound to the surface in the form of acidic or basic functional groups. The amount of surface oxides and their composition depend on the production process and an eventual aftertreatment. Furnace blacks and thermal blacks, which have been produced in a reducing atmosphere, contain about 0.2–2.0 wt % oxygen in the form of almost pure, basic surface oxides. Gas and channel blacks, which are manufactured in the presence of air, contain up to 8 wt % oxygen. In this case, the greater part of the oxygen is contained in acidic surface oxides and only a small portion in basic oxides. The amount of acidic surface oxides can be increased by oxidative aftertreatment, in which oxygen contents of up to 15 wt % can be obtained.

The surface oxides are destroyed at high temperatures. Due to this fact the weight loss at 950 °C ("volatiles") is a rough indication of the oxygen content of a carbon black.

The pH measured in an aqueous slurry is another indication of the degree of oxidation. In general, the pH is > 7 for furnace blacks (low oxygen content, basic surface oxides), 4–6 for gas blacks, and 2–4 for oxidized carbon blacks (high oxygen content, acidic surface oxides with a high amount of polar functional groups). Further organic reactions, e.g., alkylation, halogenation, esterification, can be carried out with the surface oxides to modify the surface properties.

Oxidation Behavior. Industrial carbon blacks do not spontaneously ignite when stored in air at 140 °C according to IMCO Code [417]. When ignited in air, carbon black glows slowly. In contrast to coal, dust explosions are not observed under normal test conditions [418]. However, ignition sources of extremely high energy, e.g., a gas explosion, may induce a secondary dust explosion in air.

For modification of the application properties with regard to surface oxidation, see Section 6.4.7.

6.3. Raw Materials

Mixtures of gaseous or liquid hydrocarbons which can be vaporized represent the raw materials preferable for the industrial production of carbon black. Since aliphatic hydrocarbons

give lower yields than aromatic hydrocarbons, the latter are primarily used. The best yields are given by unsubstituted polynuclear compounds with 3–4 rings. Certain fractions of coal tar oils and petrochemical oils from petroleum refinement or the production of ethylene from naphtha (aromatic concentrates and pyrolysis oils) are materials rich in these compounds. These aromatic oils, which are mixtures of a variety of substances, are the most important feedstocks today. Oil on a petrochemical basis is predominant. A typical petrochemical oil consists of 10–15 % monocyclic, 50–60 % bicyclic, 25–35 % tricyclic, and 5–10 % tetracyclic aromates.

Important characteristics determining the quality of a feedstock are the C/H ratio as determined by elemental analysis and the BMCI [419] (Bureau of Mines Correlation Index), which is calculated from the density and the mid-boiling point or from the density and the viscosity. Both C/H ratio and BMCI values give some information on the aromaticity and therefore the expected yield. Further characteristics are viscosity, pour point, temperature of solidification, alkaline content (due to its influence on the carbon black structure), and sulfur content, which should be low because of environmental and corrosion considerations.

Natural gas, which was previously the predominant feedstock for the production of channel blacks and furnace blacks in the United States, has lost its importance for economic reasons. Only thermal blacks are produced with natural gas. However, natural gas is still the most important fuel in the furnace black process, although other gases and oils are used in some cases. In several patents, recycled tail gas, in combination with oxygen or oxygen-enriched air, has also been proposed as a fuel, but has not gained any commercial importance.

Acetylene, due to its high price, is used only for the production of highly specialized conductivity blacks and battery blacks.

6.4. Production Processes

A summary of the most important production processes is given in Table 22. In general, the processes are divided into two groups: those employing partial combustion and those based on pure pyrolysis. This nomenclature is somewhat

misleading insofar as the carbon black resulting from the partial combustion process is also formed by pyrolysis. The two types of processes differ in that air is used in the one to burn part of the feedstock, thus producing the energy required to carry out the pyrolysis, whereas in the other heat is generated externally and introduced into the process.

Table 22. Summary of the manufacturing processes and feedstocks for the production of carbon black

Chemical process	Manufacturing process	Feedstock
Incomplete combustion	furnace black process	petrochemical oils and coal tar oils
	Degussa gas black process	coal tar oils
	channel black process	natural gas
	lamp black process	petrochemical and coal tar oils
Thermal cracking	thermal black process	natural gas, oil
	acetylene black process	acetylene

The furnace black process is currently the most important production process. It accounts for more than 95 % of the total worldwide production. The advantages of the furnace black process are its great flexibility, which allows the manufacture of various grades of carbon black, and its better economy compared to other processes. The following comparison makes this apparent: for similar grades of carbon black, the production rate of one flame is ca. 0.002 kg/h for channel black, ca. 0.2 kg/h for gas black, and ca. 2000 kg/h for a modern furnace black reactor. However, in spite of the more advantageous furnace black process, the production processes listed in Table 22 (except for the channel black process) are still in use for the production of special carbon blacks which cannot be obtained via the furnace black process.

6.4.1. Furnace Black Process

In the past decades, the rapidly expanding automobile industry required increasing numbers of tires with various characteristics. This led not only to the development of new rubber grades, but also to the development of new carbon blacks required by the increasingly refined application processes and to the development of a new and better manufacturing process, the furnace black process. Unlike the old channel black process,

this process allows the production of virtually all grades of carbon black required by the rubber industry. It also meets the high economic and ecological requirements of our times.

The furnace black process was developed in the United States in the 1920s, and since then, it has been greatly refined. It is a continuous process, carried out in closed reactors, so that all inputs can be carefully controlled [420]. Today most semireinforcing rubber blacks (carcass or soft blacks), with specific surface areas of 20–60 m²/g, and the active reinforcing blacks (tread or hard blacks; see Table 25), with specific surface areas of 65–150 m²/g, are manufactured by this process, as well as an increasing number of pigment-grade carbon blacks with much higher specific surface areas and smaller particle sizes. In addition to the specific surface area, other quality specifications such as structure, as measured by DBP absorption, and application properties such as abrasion resistance, modulus, and tear strength for usage in rubber, or jetness and tinting strength for color blacks, can also be systematically varied in the furnace black process by adjusting the operating parameters. This flexibility is necessary to meet the very narrow specifications required by customers.

The heart of a furnace black production plant is the furnace in which the carbon black is formed. The feedstock is injected, usually as an atomized spray, into a high-temperature zone of high energy density which is achieved by burning a fuel (natural gas or oil) with air. The oxygen, which is in excess with respect to the fuel, is not sufficient for complete combustion of the feedstock, the majority of which is therefore pyrolyzed to form carbon black at 1200–1900 °C. The reaction mixture is then quenched with water and further cooled in heat exchangers, and the carbon black is collected from the tail gas by a filter system.

Figure 56 shows a schematic drawing of a furnace black production line. The feedstock, preferably petrochemical or carbochemical heavy aromatic oils, some of which begin to crystallize near ambient temperature, is stored in heated tanks equipped with circulation pumps to maintain a homogeneous mixture. Oil is conducted to the reactor by means of rotary pumps via heated pipes and a heat exchanger, where it is heated to 150–250 °C to obtain a viscosity appropriate for atomization. Various types

of spraying devices are used to introduce the feedstock into the reaction zone. An axial oil injector with a spraying nozzle which produces a hollow-cone spray pattern, is often used. One- and two-component atomizing nozzles [421] are in use, air and steam being the preferred atomizing agents in the latter case. In other reactors, however, the feedstock is injected as a plurality of coherent or atomized streams into the accelerated combustion gases perpendicular to the direction of stream [422].

As the carbon black structure may be reduced by the presence of alkali metal ions in the reaction zone [423], alkali metal salts, preferably aqueous solutions of potassium hydroxide or potassium chloride, are often added to the make oil in the oil injector. Alternatively, the additives may be sprayed separately into the combustion chamber. In special cases, other additives, e.g., alkaline-earth metal compounds which increase the specific surface area are introduced in a similar manner.

The high temperature necessary for pyrolysis is obtained by burning fuel in excess air in a combustion chamber. Natural gas is still the fuel of choice, but other gases, e.g., coke oven gases or vaporized liquid gas, are occasionally used. Various oils, including the feedstock, are occasionally used as fuel for economic reasons. Depending on the type of fuel, special burners are used to obtain fast and complete combustion.

The air required for combustion is compressed by rotating piston compressors or turbo blowers. The air is preheated in heat exchangers by the hot carbon-black-containing gases leaving the reactor. This saves energy and thus improves the carbon black yield. Preheated air temperatures of 500–700 °C are common.

Important progress has been made on the reactor throughput: A production plant with a capacity of 20 000 t/a (2.5 t/h) was originally run with as many as 12 furnaces. In the last decades they have been replaced by a single high-performance reactor for the same capacity. Modern plants are a one-stream configuration with one unit for each process step (reactor, collecting system, pelletizer, dryer). From a technical point of view, even larger units could be built. However, due to the great variety of carbon black grades required, the capacity of one unit is economically limited by the frequency of switching over to other grades and the amount of

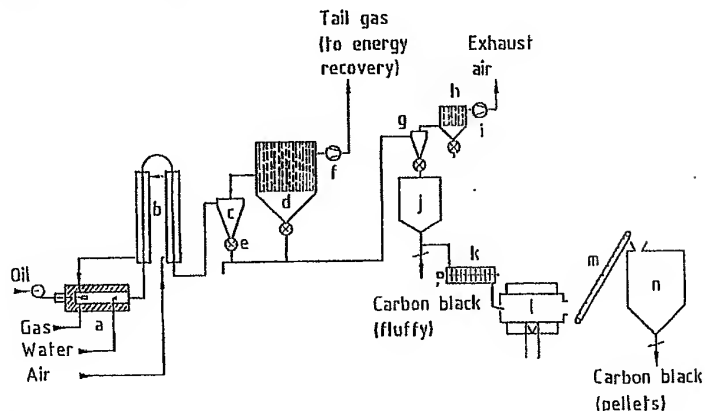


Figure 56. Furnace black process

a) Furnace black reactor; b) Heat exchanger; c) Collecting or agglomerating cyclone; d) Bag filter; e) Carbon black outlet pneumatic conveying system; f) Tail gas blower; g) Collector; h) Exhaust air filter; i) Blower for the pneumatic conveying; j) Fluffy black storage tank; k) Pelleitizer; l) Dryer drum; m) Conveying belt; n) Storage tank for carbon black pellets

off-grade carbon black which may be produced during this procedure.

The reactors of modern furnace plants vary considerably in internal geometry, flow characteristics, and the manner in which fuel and feedstock are introduced. Nevertheless, they all have the same basic process steps in common: producing hot combustion gases in a combustion chamber; injecting the feedstock and rapidly mixing it with the combustion gases, vaporizing the oil, pyrolyzing it in the reaction zone, and rapidly cooling the reaction mixture in the quenching zone to temperatures of 500–800 °C.

Schematic drawings of some typical modern furnace black reactors are shown in Figure 57. They all have a gas-tight metal jacket. The reaction zone is coated with a ceramic inner liner, generally on an alumina base, which is stable to temperatures of ca. 1800 °C. Several quenching positions allow the effective reaction volume of the reactor to be adjusted. This allows variation of the mean residence time of the carbon black at the high reaction temperature. Typical residence times for reinforcing blacks are 10–100 ms.

Most furnace black reactors are arranged horizontally. They can be up to 18 m long with an outer diameter of up to 2 m. Some vertical reactors are used especially for the manufacture of certain semireinforcing blacks [426] (Fig. 58). For further reactors, see [427].

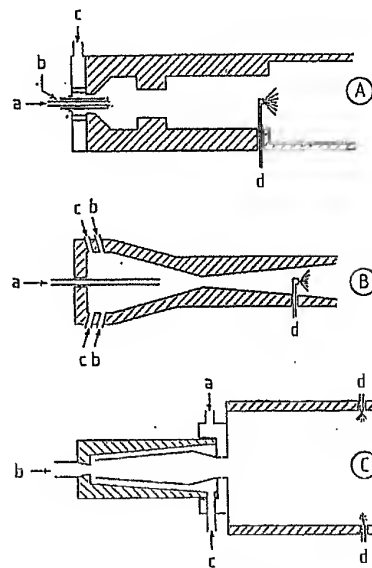


Figure 57. Furnace black reactors

A) Restrictor ring reactor; B) Venturi reactor [424]; C) Reactor with high-speed combustion chamber [425] a) Feedstock; b) Fuel; c) Combustion air; d) Quench

The properties of carbon blacks depend on the ratios of fuel, feedstock, and air, which therefore must be controlled carefully [428]. The particle size of the carbon black generally decreases with increasing amounts of excess air relative to the amount needed for the complete combustion.

tion of the fuel. Since the excess air reacts with the feedstock, a greater amount of air leads to higher oil combustion rates, resulting in rising temperatures in the reaction zone. As a consequence, the nucleation velocity and the number of particles formed increase, but the mass of each particle and the total yield decrease. This allows semireinforcing carbon blacks to be manufactured with better yields than active reinforcing carbon blacks.

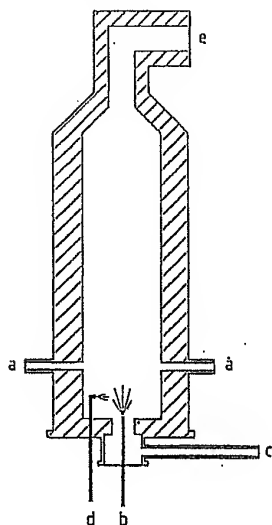


Figure 58. Vertical reactor for manufacturing semireinforcing blacks

a) Fuel inlet; b) Oil injector; c) Air conduit; d) Water spray; e) Outlet to the collecting system

The yields, which depend on the carbon black type and the type of feedstock, range between 50 and 65 % for semireinforcing blacks and 40 and 60 % for reinforcing blacks. High-surface-area pigment blacks with markedly smaller particle size than rubber blacks give lower yields.

Other parameters influencing carbon black quality are the manner in which the oil is injected, atomized, and mixed with the combustion gases, the type and amount of additives, the preheating temperature of the air, and the quench position. As long as the carbon black is in contact with the surrounding gases at the high reaction temperature, several reactions on the carbon surface occur (e.g., Boudouard reaction, water gas reaction), so that the chemical nature of the carbon black surface is modified with increasing

residence time. When quenched to temperatures below 900 °C, these reactions are stopped and a certain state of surface activity is frozen. Carbon black surface properties can also be further modified by varying the pelletizing and drying conditions (see below).

Typical processing data for reactors with a carbon black output of 10 000 t/a (1250 kg/h) of tread black and of 14 000 t/a (1750 kg/h) of carcass black are listed in Table 23. These data show that the total mass put through the reactor amounts to 10–16 t/h. Although this is done at high streaming velocities (up to 800 m/s) and high temperatures (up to 1800 °C), modern high-performance reactors can have lifetimes of two years and more.

The mixture of gas and carbon black leaving the reactor is cooled to 250–350 °C in heat exchangers by counterflowing combustion air and then conducted into the collecting system. Formerly, a combination of electroflocculators and cyclones or cyclones and filters were used [420], [429]. Currently, simpler units are preferred. Generally, the collecting system consists of only one high-performance bag filter with several chambers, which are periodically purged by counterflowing filtered gas or by pulse jets. Occasionally, an agglomeration cyclone is installed between the heat exchanger and the filter. Depending on the capacity of the production unit, the filter may contain several hundred bags with a total filter area of several thousand square meters. Usual filter loads are on the order of $0.2\text{--}0.4\text{ m}^3\text{ m}^{-2}\text{ min}^{-1}$. Since the filtered gas contains 25–40 vol % water vapor, most filters operate at temperatures above 200 °C to avoid condensation. The residual carbon black content in the off-gas is less than 10 mg/m³.

Because of the reducing atmosphere and the high temperatures in the reactor, the tail gas, which consists of 25–40 vol % water vapor, 40–50 vol % nitrogen, and 3–5 vol % carbon dioxide, also contains a certain amount of combustible gases, the amount of which depends on the feedstock and the processing conditions. These gases include 5–10 vol % carbon monoxide, 5–10 vol % hydrogen, and small amounts of methane and other hydrocarbons. The lower heating value lies between 1700 and 2100 kJ/m³. The energy remaining in the tail gas can be calculated by using the typical overall energy balance of the furnace black process shown in Fig-

Table 23. Processing data for high-performance furnace black reactors

		Semireinforcing carbon black	Reinforcing carbon black
Natural gas	m ³ /h	300–550	280–440
Air	m ³ /h	7 000–10 000	6 000–7 500
Oil	kg/h	2 500–3 300	2 000–3 000
Carbon black	kg/h	1 500–2 000	1 000–1 500
Yield	t/t kg/100 kg of oil	12 000–16 000 50–65	8 000–12 000 40–60

ure 59. The gas must be burned for environmental reasons, and its energy is used, e.g., for heating dryer drums or for the production of steam and electricity.

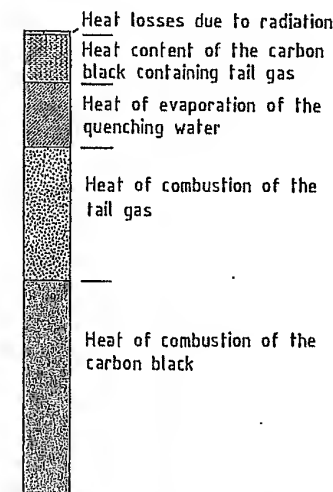


Figure 59. Typical energy balance for the manufacture of a reinforcing black

The fluffy carbon black coming out of the filter is pneumatically conveyed into a first storage tank. Small amounts of solid impurities ("grit," e.g., iron, rust, or coke particles) are either removed by magnets and classifiers or milled to an appropriate consistency.

Freshly collected carbon black has an extremely low bulk density of 20–60 g/L. To facilitate handling and further processing by the customer, it must be compacted. Densification by "outgassing"—a process by which the carbon black is passed over porous, evacuated drums—is the weakest form of compacting and allows the carbon black to retain its powdery state [430]. This form of compacting is used for

certain pigment blacks which must retain easy dispersibility.

Other pigment blacks and the rubber black are compacted by granulation. Two processes are used: dry and wet pelletization.

Dry pelletizing is a simple and energy-saving method, but it does not work with all types of carbon black. It is mainly used for color black. Dry pelletization is carried out in rotating drum where the powdery carbon black rolls to form small spheres.

The wet pelletization process is used for the majority of rubber blacks. Carbon black, water and small amounts of additives (e.g. molasses, lignosulfonates) are mixed in special pelletizers [431]. They usually consist of a horizontal cylinder ca. 3 m long and 0.7–1 m in diameter, in the axis of which a pin shaft rotates at 300–750 rpm (Fig. 60). The water containing the pelleting agents dissolved in it is injected via spray nozzles. The density of the pelletized material is ca. 10 times that of the original carbon black. DBP absorption is also reduced during this process. The pellet crush strength and some application properties in rubber can be influenced by the type and amount of the pelletizing agent. The size of the pellets is ca. 1–2 mm.

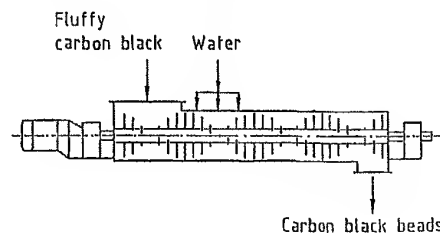


Figure 60. Pelletizing machine

The carbon black leaving the pelletizing machine contains ca. 50 wt % water. It is dried in dryer drums indirectly heated by burning tail

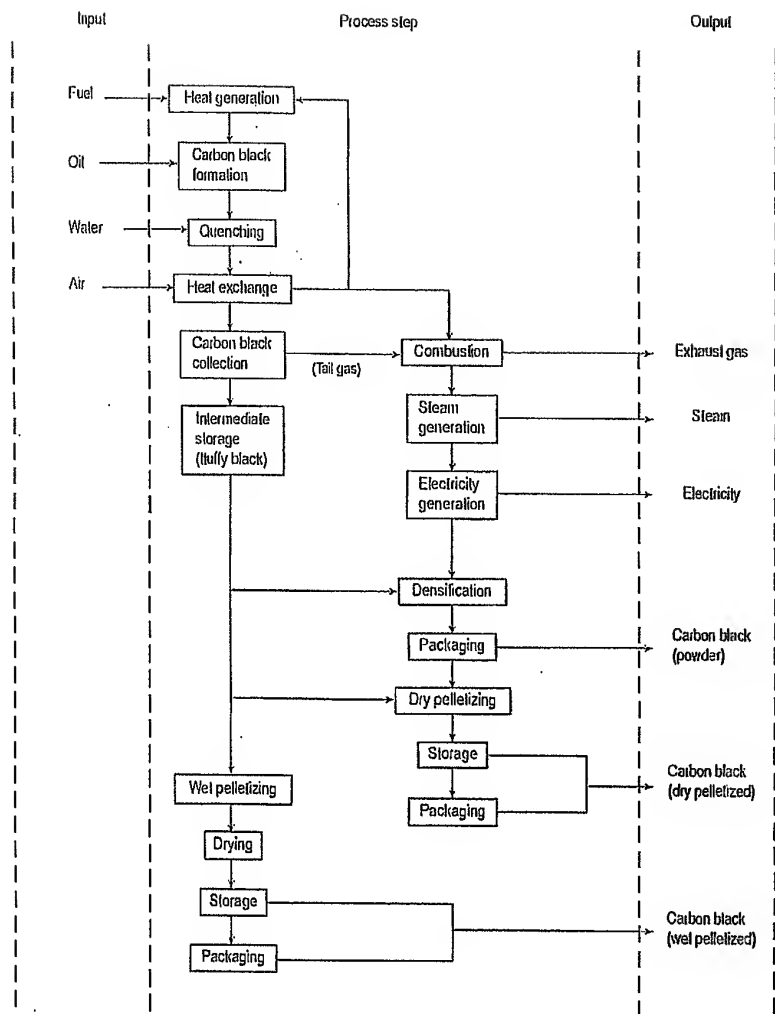


Figure 61. Furnace black process

gas. Dryer drums with a capacity of 2000 kg of carbon black per hour are 15–20 m long and 2–3 m in diameter. They are rotated at 5–15 rpm. Drying temperatures, generally between 150 and 250 °C, allow further modification of the carbon black properties.

The dried carbon black is transported via conveyor belts and elevators to the storage tank or packing station. Bulk densities of wet-pelletized carbon blacks are between 250 and 500 g/L.

A flow diagram summarizing the complete furnace black process is shown in Figure 61.

6.4.2. Gas Black and Channel Black Processes

The channel black process, used in the United States since the late 1800s, is the oldest process for producing small-particle-size carbon blacks on an industrial scale. Originally, the first reinforcing blacks were also produced by this process. In 1961, world production of channel black was about 120 000 t. Due to low profitability and environmental difficulties, the last production plant in the United States was closed in

1976. Natural gas was used as the feedstock. The carbon black yield was only 3–6 %.

In Germany, where natural gas was not available in sufficient amounts, the gas black process was developed in the 1930s. It is similar to the channel black process, but uses coal tar oils instead of natural gas. Yields and production rates are much higher with oil-based feedstock; this process is still used to manufacture high-quality pigment blacks with properties comparable to those of channel blacks. The gas black process has been used by Degussa on an industrial scale since 1935.

Originally, gas black was primarily used for the reinforcement of rubber. Today, almost all grades are used as color blacks in printing inks, plastics, lacquers, and coatings. High-quality oxidized gas blacks are of special interest, e.g., in deep black lacquers and coatings.

In the gas black process (Fig. 62), the feedstock is partially vaporized. The residual oil is continuously withdrawn. The oil vapor is transported to the production apparatus by a combustible carrier gas (e.g., hydrogen, coke oven gas, or methane). Air may be added to the oil–gas mixture for the manufacture of very small particle size carbon black. Although this process is not as flexible as the furnace black process, various grades of gas black can be made by varying the relative amounts of carrier gas, oil, and air. The carbon black properties are also influenced by the type of burners used.

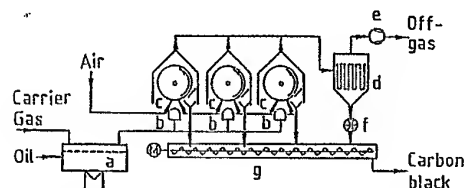


Figure 62. Degussa gas black process
a) Oil evaporator; b) Burner; c) Cooling drum; d) Bag filter; e) Blower; f) Rotary valve; g) Conveying screw

A gas black apparatus consists of a burner pipe approximately 5 m long, which carries 30–50 diffusion burners. The flames burn in contact with a water-cooled drum, where about half of the carbon black formed is deposited. This black is continuously scraped off and transported by a screw to a pneumatic conveying system. The gas black apparatus is surrounded by a

steel housing open at the bottom. At the top, fans extract the off-gas into filters, which collect the carbon black suspended in the gas. The amount of air entering the apparatus can be regulated by valves in the exhaust pipes.

Several gas black apparatus are combined to form one production unit. The whole “group” is fed by one oil vaporizer. The production rate and the yield of an apparatus depend on the grade of carbon black produced. For a typical RCC black, the production rate is 7–9 kg/h and the yield is 60 %. The yield for high-quality color blacks is considerably lower (10–30 %).

To remove possible impurities, the gas black is classified and then densified, pelletized, or submitted to an oxidative aftertreatment (see Section 6.4.7), depending on its intended use. Since gas blacks are formed in the presence of excess air, their surface is oxidized. Acidic surface oxides are predominant.

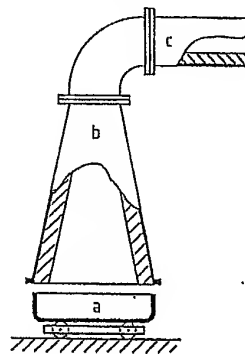


Figure 63. Lamp black process
a) Vessel filled with feedstock; b) Conical exhaust pipe; c) Pipe leading to the collecting system

6.4.3. Lamp Black Process

The lamp black process is the oldest industrial-scale production process [420], [429].

Currently, only a few plants still produce rather coarse blacks (mean particle diameter ca. 100 nm) with special properties. They are used as nonreinforcing or semireinforcing blacks in rubber goods and as tinting black with a low pigment separation tendency.

The lamp black process is only partially continuous. The feedstock—oil with a high aromatic hydrocarbon content—is burned in flat steel vessels up to 1.5 m in diameter (Fig. 63). The oil is

continuously introduced into the vessel to keep a constant feedstock level. The off-gas containing carbon black is sucked into a conical exhaust pipe, which is coated with a ceramic inner liner and leads to the cooling and collecting system. The properties of the carbon black can be influenced to some extent by variation of the distance between the vessel and the exhaust and the amount of air sucked into the apparatus. One lamp black apparatus can produce 100 kg/h. The production process must be interrupted at certain time intervals to remove coke-containing residues from the vessels.

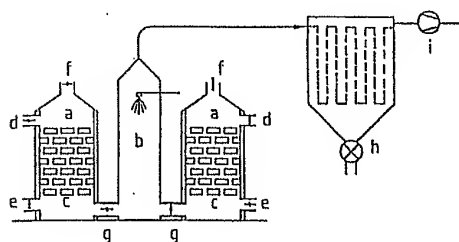


Figure 64. Thermal black process

a) Thermal black reactor; b) Cooler; c) Filler bricks; d) Inlet for the feedstock; e) Inlet for the fuel; f) Outlet for the burned fuel; g) Outlet for the pyrolysis products; h) Carbon black outlet; i) Blower

6.4.4. Thermal Black Process

Some special processes for producing carbon black are based on the thermal decomposition of lower gaseous hydrocarbons in the absence of air.

The thermal black process, which was developed in the 1930s, is still used for the production of coarse carbon blacks (nonreinforcing carbon blacks) for special applications in the rubber industry. Contrary to the above described processes, energy generation and the pyrolysis reaction are not carried out simultaneously.

A thermal black plant consists of two furnaces, which are used in alternate heating and production periods of ca. 5-min duration (Fig. 64). Each of the cylindrical furnaces (4 m in diameter and 6 m high) contains a network of heat-resistant bricks. They are heated with natural gas and air. At a temperature of ca. 1400 °C, the air is switched off and only feedstock is introduced for pyrolysis. Since this re-

action is endothermic, the temperature falls. At about 900 °C, a new heating period is necessary.

The products leaving the furnace, carbon black and nearly pure hydrogen, are cooled by injecting water into an ascending channel. The carbon black is separated in the collecting system.

Carbon blacks of lower particle size can be produced by diluting the natural gas with recycled hydrogen. Fine thermal blacks (FT blacks) with mean primary particle sizes of 120–200 nm were manufactured in this way in the past. Medium thermal blacks (MT blacks) with mean particle sizes of 300–500 nm are still produced and are obtained by using undiluted feedstock. The yield of MT blacks is about 40 % with respect to the total amount of feedstock and fuel used.

Thermal blacks are used for mechanical rubber goods with high filler contents. Cheaper products (clays, milled coals, and cokes), however, have become increasingly important as substitutes for economic reasons. The total production of thermal blacks is, therefore, decreasing.

6.4.5. Acetylene Black Process

Acetylene and mixtures of acetylene with light hydrocarbons are the raw materials for a process that has been used since the early 1900s. Unlike other hydrocarbons, the decomposition of acetylene is highly exothermic ($\Delta H = -230$ kJ/mol).

The discontinuous explosion process is the oldest technical process. It was mainly used for the production of color blacks. Continuous processes were later developed with production rates up to 500 kg/h [432]. Acetylene or acetylene-containing gases are fed into a preheated, cylindrical reactor with a ceramic inner liner. Once ignited, the reaction is maintained by the decomposition heat that is evolved. The carbon black is collected in settling chambers and cyclones. Approximately 95–99 % of the theoretical yield is obtained.

The primary particles of acetylene black have different shapes than those of other carbon blacks (Fig. 65). As the increased order in the *c* direction of the crystalline regions indicates, folded sheets of carbon layers are the main structural component. Because of their relatively

high price, the application of acetylene blacks is limited to special uses, e.g., in dry cells. Total worldwide production is ca. 40 000 t/a.

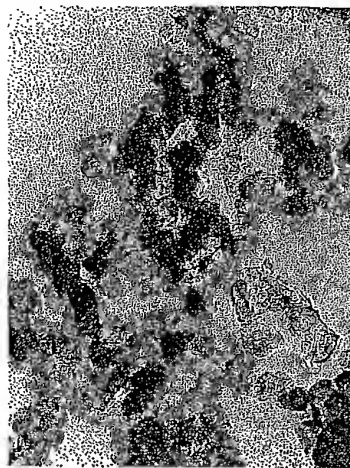


Figure 65. Electron micrograph of acetylene black

6.4.6. Other Manufacturing Processes

In a plasma, hydrocarbon vapors may be almost quantitatively decomposed into carbon and hydrogen [433]. Many producers of carbon black have done research in this field. According to numerous patent specifications, this method can be used to make small-particle carbon blacks with new properties. However, an economical plasma-based commercial process is not yet known.

The Hüls electric arc process was the only large-scale process using plasma reactions in which large quantities of carbon black were produced as a byproduct of the production of acetylene. The particles of the Hüls arc carbon black resemble those of acetylene black. The mean primary particle size is ca. 35 nm. Today, this kind of carbon black is no longer used as a pigment.

Since the price of both feedstocks and fuels, and thus, the profitability of the carbon black production processes, is highly dependent on the petrochemical industry, several attempts have been made to find new raw materials. Processes for obtaining carbon black directly from coal [434] or for isolating carbon black from used tires, for example, have been studied. None of them, however, has been of any commercial importance up to now. On the other hand, clay,

milled coal, and coke have found limited use as substitutes for very coarse carbon blacks, mainly thermal blacks and some SRF blacks. Increasing use of precipitated silicas in tire mechanical rubber goods, mostly in combination with organosilane coupling agents, which originally was indicative of an increasing search for new non-oil-based fillers, has led to new properties.

6.4.7. Oxidative Aftertreatment of Carbon Black (Fig. 66)

Oxygen-containing functional groups on the surface of carbon blacks strongly influence their application properties. High contents of volatile, i.e., high concentrations of surface oxides, increase the vulcanization rate and improve flow characteristics of inks. The gloss of papers and coatings is increased, the color is shifted from brownish to bluish, and jet often increases.

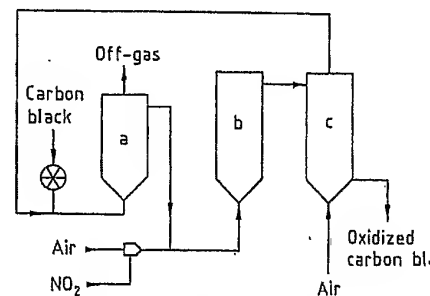


Figure 66. Equipment for the oxidative aftertreatment of carbon black in a fluidized bed
a) Fluidizing vessel; b) Reaction vessel; c) Desorption vessel

Due to the production conditions, only blacks (and channel blacks) are covered to a certain extent with acidic surface oxides. Further blacks contain only small amounts of oxygen in the form of basic surface oxides.

To amend their color properties, some carbon blacks are aftertreated by oxidation on a commercial scale. Depending on the oxidizing agent and the reaction conditions selected, different types of surface oxides are formed in varying quantities.

The simplest method of oxidizing the carbon black surface is by aftertreating it with

at 350–700 °C. However, the degree of oxidation is limited. Higher contents of surface oxides and better process control are achieved with nitric acid [435], mixtures of NO₂ and air [436], ozone, or sodium hypochlorite solutions [437] as oxidizing agents. As a rule, all strongly oxidizing agents may be used, either as a gas or in solution. Most surface oxidations of carbon black are carried out at elevated temperatures.

Oxidized carbon blacks may contain up to 15 wt % oxygen. They are strongly hydrophilic. Some of them form colloidal solutions spontaneously in water. In polar printing ink systems, lacquers, and coatings, a better wettability and dispersibility is achieved through surface oxidation [438], thus reducing binder consumption.

Surface oxidation of carbon black with nitric oxide and air can be carried out industrially in a fluidized-bed reactor [436]. A suitable aftertreatment unit consists of a preheating vessel, in which the carbon black is fluidized and heated, a reaction vessel to carry out the surface oxidation, and a desorption vessel, in which adsorbed nitric oxide is removed. Typical reaction temperatures lie between 200 and 300 °C. Depending on the degree of oxidation, the residence time can amount to several hours. The nitric oxide acts primarily as a catalyst, the oxygen in the air being the genuine oxidizing agent.

Oxidation of powdery black with ozone is also carried out on a commercial scale. Another common method of surface oxidation was carried out during pelletization. Instead of water, nitric acid was used as pelletizing agent. The surface was oxidized while the wet beads were dried at elevated temperature [439].

6.4.8. Environmental Problems

The furnace black process, the most economical and commercially advanced production method for carbon black, does not form toxic solid or liquid byproducts under normal operating conditions. The tail gas containing hydrogen and carbon monoxide was formerly emitted into the atmosphere, but is now burned, the energy being used partially within the process itself, e.g., for heating dryer drums in the wet-pelletizing process and for generating steam or electricity, so that emissions of carbon black and inflammable gases are avoided.

Although their economic importance is decreasing, progress with respect to environmental problems has also been made for the older processes that are still in use.

6.5. Testing and Analysis

The chemical composition of carbon blacks (see Section 6.2), as determined by common elemental analysis methods, is of little significance for predicting their properties. Special characteristic properties are, therefore, determined for the characterization and quality control of carbon blacks. Traces of heavy metals are determined spectroscopically in the ash. Copper and manganese ions, etc., are of special interest to the rubber industry because of their interference with the aging process in rubber goods.

Electron Microscopy. Electron microscopy is one of the most important physical methods for the characterization of finely divided solids. It allows direct viewing of the shape and morphology of particles in this order of magnitude, primary particle size, particle size distribution, and aggregation.

To determine the mean primary particle size and particle size distribution, the diameters of 3000–5000 particles are measured on electron micrographs of known magnification. Spherical shape is anticipated for calculations. However, since the primary particles generally build up larger aggregates, the results may be somewhat uncertain. The specific "electron microscopic surface area" can be calculated from the primary particle size distribution. This value refers only to the outer (geometrical) surface of the particles. For porous carbon blacks the electron microscopic surface area is lower than the specific surface area according to BET (see below).

An attempt was made to find characteristic values for the type and degree of aggregation using electron micrographs [440]. However, neither visual comparisons with standard aggregates nor automatic picture analyses have led to a practical method for a quantitative characterization of the carbon black structure on a routine basis.

High-resolution phase-contrast pictures and X-ray diffraction are used to elucidate the internal structure of single primary particles.

Sorption Analysis. Specific surface areas and porosity can be calculated from the adsorption isotherm of nitrogen at -196°C . The BET method [441] is generally accepted for the evaluation of specific surface area (m^2/g). The two-parameter equation is applicable to carbon black. The BET surface area comprises the outer surface area as well as the surface area of the pores. The outer surface area can be calculated from the adsorption isotherm by using the de Boer t -plot method.

Porosity of carbon blacks can be detected by the de Boer t -plot method [442]. The total surface area and the geometrical surface area outside the pores can be determined separately. Special attention must be paid to the selection of a suitable master t curve. Due to the small diameters of most carbon black primary particles, methods for the determination of mesopores are of no importance.

Special Analytical Test Methods. Test methods which on the one hand resemble certain physicochemical methods, but on the other hand already give some indication of application properties are summarized as special analytical test methods in Table 24. They can be carried out within a short time and are used for characterization as well as production control. Since the results are influenced by the test conditions, these test methods are standardized.

Application Tests. Physicochemical and special analytical test methods allow the classification of carbon blacks and a rough estimation of their application properties. Exact data on the application properties of a carbon black in a special system, e.g., plastic material or a rubber mixture, can only be given by application tests under nearly practical conditions.

6.6. Storage and Transportation

The majority of the carbon black produced (up to 80 %) is transported as bulk material; the rest is handled in bags. Generally, the large stocks of pelletized furnace blacks for the rubber industry are stored, by the producers as well as the customer, in coated steel storage tanks consisting of one or more cells with a capacity of 100–1000 t ($300-3000 \text{ m}^3$). Carbon black is shipped in containers or silo trucks with a capacity of up to 20 t. Recently, big bags and steel bins with a capac-

ity of up to about 1 t have gained in importance. Smaller amounts of rubber blacks and especially pigment blacks are stored and transported in paper or plastic bags stacked on pallets. In some cases, bags with special coatings are used.

6.7. Uses

The most important grades and groups of carbon black, some typical characteristics, and their principal applications are summarized in Tables 25 and 26. A general overview of the most important application fields is given in Figure 6.

About 90 % of the carbon black produced is used by the rubber industry as a reinforcing filler in tires, tubes, conveyor belts, cables, rubber profiles, and other mechanical rubber goods. Furnace blacks are predominantly used in rubber processing. Fine-particle-size carbon blacks (reinforcing blacks) are used for the production of rubber mixtures with high abrasion resistance (e.g., tire treads). Coarser carbon blacks (semireinforcing blacks) are used in rubber mixtures requiring low heat buildup during dynamic stress (e.g., carcass mixtures). Very coarse carbon blacks (nonreinforcing blacks) are incorporated into mixtures with high elasticity and good extrusion properties.

Table 25 lists furnace rubber blacks and their main application fields.

According to the commonly used ASTM classification (ASTM D 1765 and D 2516), rubber blacks are characterized by one letter and three-digit number. The letter indicates the influence of the carbon black on the vulcanization process (N=normal curing, and S=slow curing). The first digit of the number should characterize the primary particle size or the specific surface area (Table 27). The other two digits are free and are used to identify individual grades within the group. Within each carbon black group, considerable variation in the combination of properties is possible, e.g., by varying the carbon black structure (DBP absorption) and surface activity.

Quantitatively, the pigment blacks are substantially less important than the rubber blacks. They are used for the manufacture of printing inks, coloring plastics, fibers, lacquers, coatings, and paper (see Table 26). Oxidized carbon blacks are frequently used in the printing ink and

Table 24. Special analytical test methods for carbon black

Test method	Unit	Standard	Remark
Iodine adsorption	mg/g	ASTM D 1510; ISO 1304	amount of iodine adsorbed from aqueous solution as a measure for the specific surface area; not applicable for oxidized carbon blacks
CTAB surface area	m ² /g	ASTM D 3765; ISO 6810	amount of cetyl trimmonium bromide adsorbed from aqueous solution as a measure for the specific outer surface area
BET surface area	m ² /g	ASTM D 3037; DIN 66 131, 66 132	total specific surface area calculated from the nitrogen adsorption isotherm by using the BET equation
External surface area	m ² /g	ASTM D 5816	STSA (statistical thickness surface area) calculated from the nitrogen adsorption isotherm
Aggregate dimension		ASTM D 3849	determination of aggregate dimensions (unit length, width, etc.) by electron microscope image analysis
DBP absorption	mL/100 g	ASTM D 2414; ISO 4656; DIN 53 601	determination of the wetting point with dibutyl phthalate in a special kneader as a measure for the carbon black structure
24M4-DBP absorption	mL/100 g	ASTM D 3493; ISO 6894	determination of DBP absorption after repeated compressing at high pressure as a measure for the permanent structure
Oil absorption	%	DIN ISO 787/5	percentage of linseed oil needed to make a barely flowable paste
Jetness, blackness value		DIN 55 979	light absorption of a carbon black paste in linseed oil; determination by visual comparison against standard blacks or by measuring the absolute light remission (DIN)
Tinting strength	%	ASTM D 3265; DIN ISO 787/16, 24; DIN 53 204; DIN 53 234	ability of a carbon black to darken a white pigment in a linseed oil paste; the tinting strength is the weight percentage of the standard carbon black with respect to the tested black to obtain the same gray tone; different standard white pigments and carbon black concentrations are used according to ASTM and DIN ISO
Volatiles	%	ISO 1126; DIN 53 552	weight loss when calcined at 950 °C for 7 min
Heating loss (moisture)	%	ASTM D 1509; DIN ISO 787/2	weight loss on drying at 125 °C for 1 h (ASTM) or 2 h at 105 °C (DIN ISO)
pH		ASTM D 1512; DIN 53 200	pH of an aqueous slurry of carbon black; pH is mainly influenced by surface oxides
Extractables	%	DIN 53 553	amount of extractable material (usually by boiling toluene) in at least 8 h
Toluene discoloration		ASTM D 1618; ISO 3858	light absorption (transmission) of a toluene solution of the extracted material
Ash content	%	ASTM D 1506; DIN 53 586	amount of noncombustible material after burning the carbon black at 675 °C (DIN) or 550 °C (ASTM, DIN)
Sulfur content	%	ASTM D 1619; DIN 53 584	
Sieve residue	%	ASTM D 1514; DIN ISO 787/18	amount of coarse impurities that cannot be purged through a testing sieve by water
Pour density	g/L	ASTM D 1513; DIN 53 912	measure for the densification of carbon black
Tamped density	g/L	DIN ISO 787/11	similar to bulk density; however, void volume is reduced by tamping

Table 24. (Continued)

Test method	Unit	Standard	Remark
Pellet size distribution		ASTM D 1511	determination by means of sieve shaker
Fines content	%	ASTM D 1508; DIN 53 583	only for pelletized blacks; percentage passing through a sieve of 125 μ m mesh width
Pellet crush strength	g	ASTM D 5230; ASTM D 3313	individual pellet hardness

Table 25. Rubber blacks

ASTM No.	Iodine adsorption, mg/g	DBP absorption, mL/100 g	Use in natural and synthetic rubber
N 115	160	113	tire treads, rubber goods with high abrasion resistance (also as blend with N 220 and N 330 and N 326)
N 121	121	132	tire treads for high-performance passenger cars
N 125	117	104	tire treads for trucks, off-road tires
N 220	121	114	tire treads for trucks, tank pads, conveyor-belt covers
N 234	120	125	tire treads for high-performance cars, tank pads, conveyor belt covers
N 326	82	72	tire carcasses, steel cord adhesion compounds, mechanical rubber goods
N 330	82	102	tire treads, tire carcasses (blended with less-active carbon blacks), tire sidewalls, mechanical rubber goods
N 335	92	110	tire treads for passenger cars
N 339	90	120	tire treads for passenger cars, abrasion-resistant mechanical rubber goods
N 347	90	124	tire treads for passenger cars, abrasion-resistant mechanical rubber goods
N 351	86	120	tire treads, abrasion-resistant mechanical rubber goods
N 356	92	154	tire treads, cushion gum
N 375	90	114	tire treads for passenger cars and trucks, tank pads, conveyor-belt covers
N 539	43	111	tire carcasses, mechanical rubber goods with good dynamic properties, extrusion compounds
N 550	43	121	tire carcasses, mechanical rubber goods with good dynamic properties, extrusion compounds
N 650	36	122	tire carcasses, extrusion compounds
N 660	36	90	tire carcasses, molded goods
N 683	35	133	tire carcasses, tire sidewalls, mechanical rubber goods with good dynamic properties, extrusion compounds
N 762	27	65	mechanical rubber goods with excellent dynamic properties
N 765	31	115	tire carcasses, molded goods, extrusion compounds
N 772	30	65	mechanical rubber goods with excellent dynamic properties
N 774	29	72	tire carcasses, mechanical rubber goods with excellent dynamic properties, molded goods

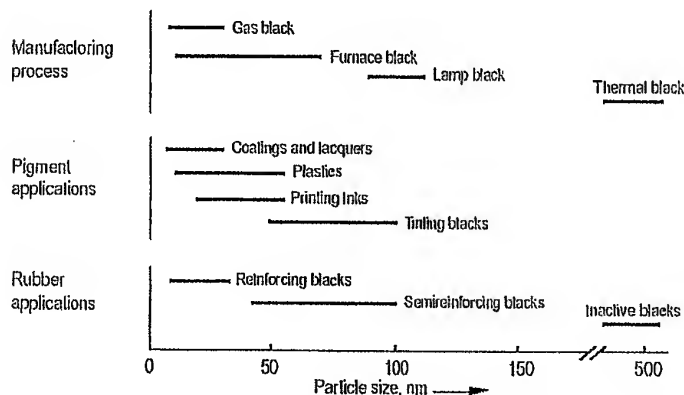


Figure 67. Mean particle sizes and typical applications of various carbon blacks

Table 26. Pigment blacks

Type *	Blackness in linseed oil	Tinting strength **, %	Volatiles, %	BET surface area, m ² /g	Mean primary particle size, nm	pH	Application
Gas black							
HCC	> 270	120-122	4-6	250-350	13-15	4-5	extremely deep
HCC ox.	> 270	112-116	15-25	300-500	13-17	2-3	black paints and coatings of all types, plastics, fibers
MCC	250-270	120-122	4-6	150-200	15-20	4-5	coatings, plastics, fibers
MCC ox.	250-270	112-118	13-18	200-300	15-20	2-4	coatings, plastics, fibers
RCC	240-250	105-115	4-6	90-110	25-30	4-5	paints, coatings, printing inks,
RCC ox.	240-250	100-110	10-15	100-200	25-30	3-4	carbon paper, carbon ribbons, plastics, fibers
Lamp black							
	208-210	25-30	1-2	18-25	90-110	7-9	tinting black for coatings and plastics
Furnace black							
HFC	> 255	115-125	0.5-1.5	250-300	14-15	9-10	high-jet coloring of plastics
MFC	250-260	120-126	0.5-1.5	150-200	16-18	9-10	high-jet coloring of plastics
RFC	240-250	95-120	0.5-1.5	80-120	20-30	9-10	plastics, printing inks,
RFC ox.	240-250	110-120	2-3	100-120	20-30	2.5-3.5	carbon paper, carbon ribbons, fibers, UV stabilization of polyolefins
LCF	215-235	60-100	0.5-1	30-65	30-60	9-10	plastics, tinting black,
LCF ox.	215-235	65-105	1.5-2.5	30-65	30-60	2.5-4	printing inks

* HCC = high color channel, MCC = medium color channel, RCC = regular color channel, HCF = high color furnace, MCF = medium color furnace, RCF = regular color furnace, LCF = low color furnace.

** Reference: IRB 3 = 100 %.

coating industry. While high-color gas blacks are still predominant in lacquers and coatings, furnace blacks are becoming more and more important in plastics, coatings, and printing inks.

Besides their two main uses as reinforcing fillers and pigments, small amounts of carbon blacks are used by the electrical industry to manufacture dry cells, electrodes, and carbon brushes. Special blacks are used to give plastics antistatic or electrical conduction properties. Another application is the UV stabilization of polyolefins [444].

Table 27. Classification of rubber blacks according to ASTM D 1765 and ASTM D 2516

Group no. (first digit of the three-digit ASTM number)	Average particle size, nm	Specific surface area*, m ² /g
0	1 - 10	> 155
1	11 - 19	125 - 155
2	20 - 25	110 - 140
3	26 - 30	70 - 90
4	31 - 39	43 - 69
5	40 - 48	36 - 52
6	49 - 60	26 - 42
7	61 - 100	17 - 33
8	101 - 200	-
9	201 - 500	-

* The ranges of the specific surface area may vary, depending on the structure of the carbon blacks.

6.8. Economic Aspects

In 1995, approximately $(6-6.5) \times 10^6$ t of carbon black was produced, and production capacity was estimated to be nearly 8×10^6 t/a (Table 28). The annual growth rate, on the average 7.9 % per annum between 1965 and 1975 in the United States, has since decreased substantially, primarily for rubber blacks due to longer tire life and the fact that the car market is reaching saturation. Therefore, the future growth rate of the carbon black market is expected to be rather limited and will not exceed 1-2 % per annum.

Table 28. Carbon black production capacity (1996)

Country or region	Capacity, 10 ³ t
North America	1815
Western Europe	1310
Eastern Europe	1545
Asia	2630
South America	480
Africa, Australia	185
Total	7965

Nearly 40 % of the total world production capacity for carbon black is concentrated in the United States and Western Europe. A detailed survey of the capacities in Western Europe given in Table 29.

More than 90 % of the total amount of carbon blacks produced are used as reinforcing fillers: rubber, of which 65-70 % go into the tire industry and an additional 25-30 % are needed for the production of mechanical rubber goods. Less than 10 % of all carbon blacks produced are used for nonrubber purposes.

Table 29. Carbon black production capacity in Europe (1995/96)

Country	Capacity, 10 ³ t
United Kingdom	180
Germany	277
France	280
Italy	200
Netherlands	160
Spain	90
Sweden	40
Others	83
Total	1310

6.9. Toxicology and Occupational Health

As far as toxicology is concerned, one must distinguish between soot, which is formed by the uncontrolled combustion of coal and oil, and carbon black, which is industrially produced under precisely defined conditions. Commercial carbon blacks are characterized by an atomic ratio H : C of < 0.1, low ash content, and high adsorption capacity. The soluble organic fraction (extractable materials) is less than 0.5 wt %.

The "chimney-sweep cancer" described by P. PORT in England as early as 1775, which is basically related to soot but not to carbon black, was the starting point of intensive research on analytical test methods for polycyclic aromatic hydrocarbons (PAH) in carbon blacks. Increasingly refined test methods have been developed (e.g., column, thin-layer, and paper chromatography, gas chromatography, HPLC, UV and fluorescence spectrophotometry, and mass spectroscopy) to detect traces of such substances and to investigate the ability of carbon black surfaces to adsorb and to desorb PAHs.

Many years of experience in the carbon black producing and processing industry have clearly

shown that there is no health hazard attributable to this product. Occasional allegations that carbon blacks impair human health have been refuted. In most cases it was possible to attribute these claims to confusion between carbon blacks and soot or coal dust. Carbon black differs markedly from soot, the unwanted, uncontrolled byproduct of combustion found in chimneys and the ambient air [445], [446].

Commercial carbon blacks (not aftertreated) consist of more than 95 % of carbon, and small amounts of hydrogen, oxygen and sulfur. They have an atomic ratio H:C of < 0.1 and a low ash content. In most carbon blacks the total toluene-extractable matter is less than 0.15 %, only part of which consists of polycyclic aromatic hydrocarbons (PAHs). Due to this low content and the highly adsorbent properties of carbon black, the extractable matter is bound very tightly on the surface and can only be removed with powerful solvents [447]. In contrast, soots vary widely in composition and properties. Besides carbon they contain variable amounts of inorganic and organic byproducts. Because of their uncontrolled genesis the content of extractable matter is often very high (> 25 %) and consists, among others, of a wide range of PAHs. The high content and loose binding of the PAHs is to a large extent responsible for the mutagenicity and carcinogenicity of soots.

Detailed studies of workers in the carbon black industry and among carbon black consumers in the United States and Europe have shown that carbon black causes neither structural damage to the lungs nor lung tumors. No association between cumulative carbon black exposure and the incidence of respiratory disease could be detected [448-450].

In small-animal tests no irritation of the mucous membranes or eyes was observed. Also no changes could be detected when the skin was exposed to carbon black. Conversely, animals exposed to the benzene extract of the same carbon black developed a significant number of malignant tumors [451]. If adsorbed on the carbon black surface, the PAHs are biologically inactive. Tests in five systems for genetic activity of a furnace black containing 294 ppm toluene-extractable PNAs indicated that no mutagenic activity could be attributed to whole carbon black [452]. The results of several studies provided no indications of pathological effects

in the gastrointestinal tracts when carbon blacks were ingested in rodents [453].

Harmful materials other than PAHs, such as polychlorinated bi- and triphenols, polychlorinated dioxins, and polychlorinated hydrofurans, were not found in carbon blacks. Nitrosamines could not be detected in carbon black, but they may be formed in rubber compounds if rubber chemicals containing secondary amines are used. The total amine content of carbon black is less than 0.01 %, and the aromatic amine content is therefore even lower. Heavy metal content does not exceed 0.002 %. Carbon blacks therefore conform to all known regulations that limit these impurities.

Lifelong inhalation studies on various species, involving titanium dioxide, iron oxide, talc, diesel soot, as well as carbon black, have shown that these fine dusts, hitherto regarded as inert are toxic to the lung [454], [455]. Of the various species used in the studies, including rats, mice and hamsters, only the rat developed identifiable lung tumors. In all cases the rats were exposed to high dust levels for prolonged periods of time, to the point that they experienced a phenomenon termed "lung overload". The effect is not restricted to carbon black. It appears from the results of long-term inhalation studies that any insoluble, low-toxicity particle will cause lung tumors in rats if deposited chronically at high enough doses [456]. Extrapolating the incidence of lung tumors in rats inhaling inert insoluble particles, such as carbon black, to human responses must be seriously questioned. The tests were carried out under such extreme overload conditions, never experienced in the workplace today, that the lungs of the rats were unable to clear themselves during nonexposure periods.

Such high carbon black levels could not occur in modern carbon black production plants. Most of the carbon black producing countries have adopted the U.S. TLV of 3.5 mg/m^3 [457]. Extensive sampling in a number of carbon black plants in Europe [458] resulted in an occupational exposure standard (OES) for carbon black of 3.5 mg/m^3 (8-h TWA) and 7 mg/m^3 (STEL). In an exhaustive review in 1984, carbon black was classified by IARC [459] in Group 3: *Not classifiable as to its carcinogenicity to humans*. This classification was confirmed in 1987. However, based on the results of the in-

halation studies with rats, IARC [460] reclassified carbon black in 1995 in Group 2B: *The agent is possibly carcinogenic to humans*. The criteria applied are: Inadequate evidence in humans and sufficient evidence in experimental animals.

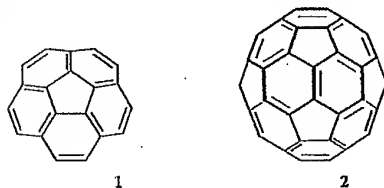
Only if strong evidence can be provided that the mechanism of carcinogenicity in rats does not operate in humans might a new reclassification of carbon black by IARC in Group 3 be possible.

Food Contact Regulations. Carbon blacks, which according to their application properties may be used for food products, cosmetics, drinking water pipes, food packaging materials, and toys, must comply with local regulations. The testing methods for the approval of carbon blacks for such applications are different in different countries. The general aim, however, is to give limitations for the content of PAHs and of heavy metals. In general, the amount of heavy metals is far below the limitations. With respect to PAHs, either the total amount of extractable materials or the content of special species is limited. Since industrial carbon blacks contain only trace amounts of strongly adsorbed PAHs, the majority of commercial grades comply with these regulations.

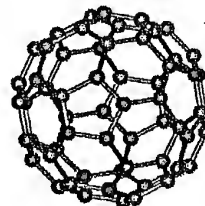
7. Fullerenes

7.1. History

It has been known since the early work of HAHN et al. on nuclear fission products [461] that in the gas phase at 3000–4000 °C under the conditions of a high-frequency arc carbon tends to form C_n clusters. Cluster ions up to C_{15} were detected [462]. In 1970 OSAWA recognized that the bowl-shaped corannulene **1** is part of a soccer-ball framework, and postulated the existence of the stable C_{60} cluster **2** [463] and discussed its possible aromatic properties [464].



In 1984 it was observed that upon laser vaporization of graphite, large all-carbon clusters C_n with $n=30-190$ can be produced [465]. Only ions with even numbers of carbon atoms were observed in the mass spectra of these carbon clusters, among which were C_{60} and C_{70} . Their identity, however, was not recognized at this time. The breakthrough came in 1985 [466] when KROTO visited the Rice University in Houston, where SMALLEY and coworkers had developed a technique [467] for generating clusters by focusing a pulsed laser on a solid (in this case graphite) and studying them by mass spectrometry. The original goal of KROTO and SMALLEY was to simulate the conditions under which carbon nucleates in red-giant stars. Under specific conditions of cluster formation, a peak attributed to C_{60} ($m/z=720$) and a less intense peak attributed to C_{70} ($m/z=840$) exhibit pronounced intensity in the spectra. Conditions were found under which the mass spectra were completely dominated by the C_{60} signal. KROTO and SMALLEY concluded that the stability of C_{60} is due to its spherical structure, that is, a truncated icosahedron with I_h symmetry (Fig. 68). The substance was named buckminsterfullerene due to its geometrical similarity with the geodesic domes constructed by the American architect BUCKMINSTER FULLER and its discovery was reported to *Nature* on September 12, 1985 [466]. Later the enhanced intensity of the peak for C_{70} , another stable fullerene, was understood. Although buckminsterfullerene C_{60} had been discovered, a method for its synthesis in macroscopic amounts remained to be found.



Buckminsterfullerene

Figure 68. Ball-and-stick model of buckminsterfullerene

The second breakthrough in the fullerene research was achieved by KRÄTSCHMER and HUFFMAN [468]. Their intention was to produce laboratory analogues of interstellar dust by vaporization of graphite electrodes in a helium atmo-

sphere [469]. At a certain helium pressure, the IR spectra of the soot generated by the vaporization of graphite showed four sharp absorptions besides the continuum of regular soot [470]. These absorptions were close to the positions predicted for buckminsterfullerene [471]. The fullerenes were isolated from the soot by sublimation or extraction. This allowed the determination of spectroscopic and crystallographic data, as well as experiments with ^{13}C -enriched material, and moved C_{60} from the world of elusive objects known only from mass spectroscopy to that of material science. Higher fullerenes can also be obtained in appreciable amounts by this technique.

The discovery of C_{60} led to an explosive growth in research into the properties of this new class of carbon allotropes. More than a thousand publications on fullerenes appear each year, dealing with their chemical and physical properties and material science aspects.

The discovery of the fullerenes was honored by the award of the Nobel prize for Chemistry in 1996 to KROTO, CURL, and SMALLEY.

7.2. Production

7.2.1. Vaporization of Graphite

Resistive Heating of Graphite. The resistive heating of graphite was the first method for producing macroscopic quantities of fullerenes [468]. The apparatus first used by KRÄTSCHMER et al. for the production of C_{60} was a bell jar connected to a pump and gas inlet. In the jar two graphite rods – one sharpened to a conical point and the other with a flat end – are kept in contact by a spring. The apparatus is evacuated, filled with 140 mbar of helium, and an electric current passed through the rods. This heats the point of contact to $2500\text{--}3000^\circ\text{C}$ and forms a black smoke, which condenses on the bell jar and a smoke catcher. The fullerenes are extracted from the soot with toluene in a yield of 10–15 %. The HUFFMAN–KRÄTSCHMER process has been patented, and the first computer-controlled, fully automated fullerene production systems are now commercially available.

More simply constructed modifications of this fullerene generator have been developed [472–474], in which vertical graphite electrodes

are fed by gravity. This, together with low costs, make them more attractive to synthetic chemists. A simple benchtop reactor gives a yield of fullerenes based on evaporated graphite in the range of 5–10 % [474].

Arc Heating of Graphite. Arc vaporization [475–477] of graphite was first developed by SMALLEY [476]. The tips of two sharpened graphite rods are kept at contact-arc distance [476], so that the electric power is dissipated in an electric arc rather than in ohmic heating. This method allows efficient evaporation of carbon; the yield of fullerenes is about 15 %. The disadvantage of this method is the intense UV radiation originating from the arc plasma. The absorption of UV light by fullerenes produces a triplet state T_1 with a lifetime of a few microseconds [478]. In the T_1 state, the fullerene is an open-shell system that can readily react with other carbon species C_n to give a nonvaporizable insoluble product [476].

Solar Heating of Graphite. The problem of intense UV radiation is avoided by the use of solar furnaces as fullerene generators [476], [478], which lead to far lower exposure of the fullerenes to radiation than arc vaporization or resistive heating. In the solar generator developed by SMALLEY [476], sunlight is focused by parabolic mirrors onto the tip of a graphite rod under an argon atmosphere in a Pyrex tube. The condensing carbon vapor quickly moves away from the intense sunlight, cools in the upper regions of the Pyrex tube, and subsequently deposits on the upper walls. Although fullerenes can be obtained in this way, the efficiency of the generator is not very high.

Inductive Heating of Graphite. Fullerenes can also be produced by direct inductive heating of a carbon sample in a boron nitride support [479]. Evaporations at 2700°C in a helium atmosphere lead to the formation of a fullerene-containing soot, which can be collected on the cooler parts of the Pyrex reactor. This method allows continuous operation by keeping the graphite sample continuously in the heating zone. The evaporation of 1 g of graphite gives 80–120 mg of fullerene extract within 10 min.

Exhibit 4

Figure 3

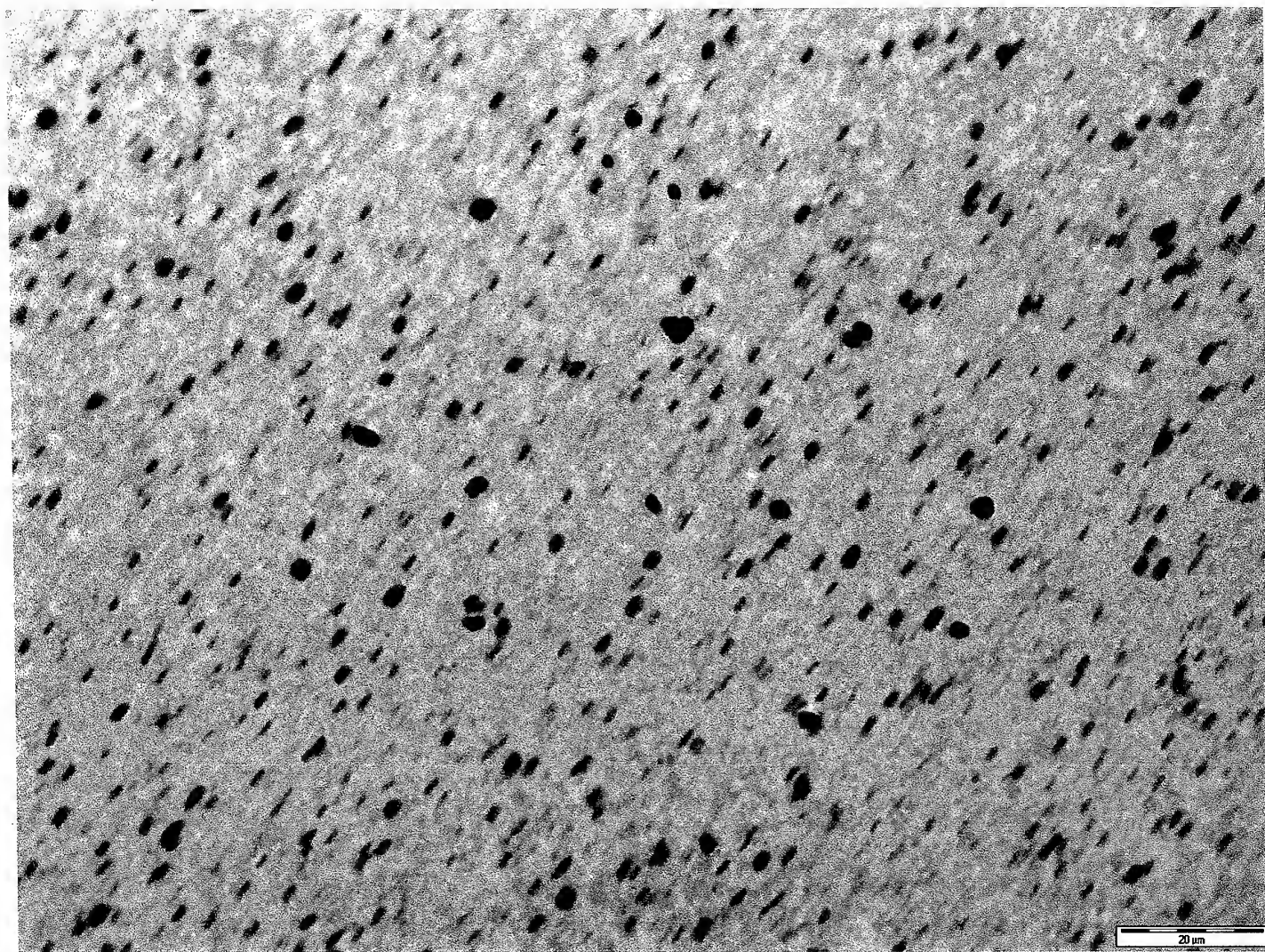


Figure 3

Exhibit 5

Declaration of Gerd Tauber with C.V.

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No. 10/627,501 Confirmation No.: 3242
Applicant(s): HEINZ ZOCH
Filed: July 25, 2003
TC/A.U. 1713
Examiner: William K. Cheung
Title: AQUEOUS, COLLOIDAL, FREEZE-RESISTANT AND STORAGE-
STABLE GAS BLACK SUSPENSION

Docket No.: 032301.341
Customer No.: 25461

MAIL STOP AMENDMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

Now comes Gerd Tauber and hereby declares and states:

I am one of the co-inventors of the above-identified U.S. Patent Application and have read and understood the above U.S. application and understand that the Examiner in the United States Patent Office has rejected the claims in the above-identified application based on the U.S. Patent 5,609,671 of *Nagasawa*. I understand that the Examiner has taken the position that it would be necessary to show the use of gas black in ink is critical in obtaining the results disclosed in the present application. The Examiner has said that it would be obvious to one of ordinary skill in the art that any carbon black would be suitable for obtaining the carbon black dispersions as claimed in this application.

For the purpose of determining whether there is a difference between gas black and other carbon blacks when used in aqueous suspensions, the following experiments were done.

The formulations used for making carbon black suspensions are shown in Table 5 attached hereto. The gas black suspension 2 is made according to the invention.

Reference suspension 6 is identical with gas black suspension 2 except that furnace black is used instead of gas black. Reference suspensions 7, 8, 9, 10 and 12 also were made with gas black but did not contain with the neutralized styrene-acrylic acid copolymer utilized by the inventors as described in this application. Reference suspensions 10 and 11 are identical except for the fact that in referenc suspension 11, a furnace black is used instead of a gas black.

Similarly, the difference between reference suspension 12 and reference suspension 13 resides in the use of a furnace black in reference suspension 13 instead of the gas black which is used in reference suspension 12. All other conditions were held constant.

The materials used in these tests is described as follows:

PVP is polyvinyl pyrrolidone from GAF. MA-CP is Tego Dispers 750W, a styrene-maleic anhydride copolymer from Tego. Fatty alcohol glycol ether sulfate is Disponil FES 3215 from Cognis. Joncryl 690 is a styrene--acrylic acid copolymer, molecular weight 16500. Joncryl 617 is a styrene--acrylic acid copolymer with a molecular weight of greater than 200,000. Joncryl 8004 is a styrene--acrylic acid copolymer with a molecular weight of 60,000. AMP 90 is 2-amino-2-methyl-1-propanol solution from Angus Chemie.

The amount of dispersion-supporting additive for each formulation was calculated on the amount of active ingredient of gas black suspension 2 according to the invention.

As shown in the accompanying photo, reference mixture 6 based on furnace black displays a poorer degree of dispersion than the gas black suspension according to the invention (see attached Fig. 3). Figures 1C and 2D show gas black suspensions of the invention.

Reference suspensions 10 and 11 could not be dispersed to form liquid pigment black dispersions. They become pasty during the dispersion process. Reference sample 13 converted to a gel a few hours after the dispersing process and is therefore undesirable.

Table 5

Sample	Gas black suspension: 2 according to the invention	Reference suspension: 6	Reference suspension: 7	Reference suspension: 8	Reference suspension: 9	Reference suspension: 10	Reference suspension: 11	Reference suspension: 12	Reference suspension: 13
Gas Black NIPex 160 IQ	15	--	15	15	15	15	--	15	--
Furnace black Printex 90	--	15	--	--	--	--	15	--	15
Joncryl 690 (35 % resin solution)	15	15	--	--	--	--	--	--	--
Joncryl 617	--	--	--	--	--	10	10	--	--
Joncryl 8004	--	--	--	--	--	--	--	15	15
MA-CP	--	--	11.25	--	--	--	--	--	--
PVP	--	--	--	4.5	--	--	--	--	--
Fatty alcohol glycol ether sulfate	--	--	--	--	15.0	--	--	--	--
Acticide MBS	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
deion. Water	69.7	69.7	73.45	80.2	69.7	74.7	74.7	69.7	69.7

Various suspension properties are summarized in Table 6 enclosed herewith.

Table 6

Sample	Reference: suspension according to the invention	Reference: suspension 6	Reference: suspension 7	Reference: suspension 8	Reference: suspension 9	Reference: suspension 10	Reference: suspension 11	Reference: suspension 12	Reference: suspension 13
Ability to produce a 15 % pigment black suspension	+	+	+	+	+	-	-	+	-
Degree of dispersion (light microscope)	+	-	-	-	+	n.d.	n.d.	-	n.d.
Average particle size [nm]	+ (92)	- (121)	- (112)	+ (98)	+ (86)	n.d.	n.d.	- (136)	n.d.
Freeze resistance	Yes	no	no	no	no	n.d.	n.d.	no	n.d.
Surface tension [mN/m]	+ (66.7)	+ (66.9)	- (58.8)	+ (70.1)	- (38.1)	n.d.	n.d.	+ (64.6)	n.d.
pH	+ (8.9)	+ (8.8)	+ (8.6)	+ (8.6)	+ (8.9)	n.d.	n.d.	+ (8.8)	n.d.
Viscosity [mPas]	+ (8.2)	+ (7.3)	+ (7.4)	+ (6.8)	+ (4.5)	n.d.	n.d.	- (17.1)	n.d.
Zeta Potential [mV]	++ (-31)	n.d.	+ (-14)	+ (-14)	n.d.	n.d.	n.d.	n.d.	n.d.
Storage Stability 50 °C/35d	+	- (sedimentation)	- (sharp rise in viscosity)	+	+	n.d.	n.d.	- (sedimentation)	n.d.

‘-’ = does not meet the requirements

‘+’ = meets the requirements

`++` = far exceeds the requirements

Table 6 measures ability to produce a 15% pigment black suspension, the degree of dispersion, the average particle size, freeze resistance, surface tension, pH, viscosity, zeta potential and storage stability. These are all important parameters when preparing carbon black dispersions. The results clearly show in Table 6 that the gas black suspension 2 according to the invention meets the conditions for forming a good product.

Table 6 shows that reference suspensions 6, 7 and 8 also form a 15% p pigment black suspension. However, these 3 reference suspensions do not meet the requirements for degree of dispersion. They also show poor freeze resistance.

Reference suspension 9 demonstrates poor freeze resistance.

Reference suspensions 10, 11 and 13 were not capable of forming a 15% pigment black suspension.

Reference suspension 12 did not meet the requirements for degree of dispersion.

Determining viscosity:

The rheological performance is measured in a rotation experiment with a constant shear rate (CSR) using a Physica USD 200 rheometer. The viscosity is read off at a shear rate of $1,000 \text{ s}^{-1}$.

Determining the average particle size:

The particle size distribution is determined using a Horiba LB-500 photon correlation spectrometer (PCS) and the "median value" displayed is read off as the average particle size. The measurement is obtained using an undiluted suspension sample.

Determining the surface tension:

The dynamic surface tension is measured using a BP 2 bubble tensiometer supplied by Krüss. The final reading is taken at 3,000 ms.

Storage stability test at 50°C over 28 days.

The samples are stored for 28 days at 50°C in a drying oven. The viscosity and sedimentation tendency are checked. A 300 ml sample of suspension is stored in a closed glass flask for 28 days at 50°C in a drying oven. The formation of sediment at the bottom is checked with a spatula and the viscosity measured with a Brookfield DV II Plus viscometer. In addition, sediment formation is tested in a number of samples stored at room temperature.

Freeze resistance test:

The samples are frozen and the degree of dispersion checked using a light microscope after thawing. A sample is judged to be freeze resistant if after being thawed, the frozen sample again has a highly liquid consistency, forms no sediment and no reagglomerations are visible under the light microscope.

The collidal gas black suspensions according to the invention in particular satisfy all the requirements of an optimum suspension. The same dispersion formulation based on furnace black (reference sample 6) or using another dispersion supporting additive (reference samples 7 and 12) did not meet the storage stability requirements. Reference sample 8 and 9 did not pass the freezing stability test.

Inks with a five percent carbon black content are prepared from the carbon black suspension samples with 2-pyrrolidone, 1, 3-propanediol, glycerine and deionised water. To this end, the premix of ink additives is prepared and the carbon black suspension carefully added with stirring. The prepared ink is filtered with a filter fineness of 500 nm. Six micron draw downs are then produced on copier paper (Kompass copy office) using a K Control Coater coating device and an optical density measured after 24 hours using a densitometer.

Printing tests were performed using a Canon BJC-S450 office printer. To this end the ink is first deaerated under vacuum and introduced into a cleaned original printer cartridge.

The results are presented in Table 7.

Table 7

Sample	Gas block suspension 11.2.10 according to the invention	Reference suspension 5	Reference suspension 7	Reference suspension 8	Reference suspension 9	Reference suspension 10	Reference suspension 11	Reference suspension 12	Reference suspension 13
Light microscope	+	0	0	0	0	n.d.	n.d.	0	n.d.
pH	8.7	8.6	8.7	8.6	8.7	n.d.	n.d.	8.8	n.d.
Viscosity 23°C [mPas]	3.1	3.3	3.3	3.2	3.1	n.d.	n.d.	3.8	n.d.
	46	48	45	46	40	n.d.	n.d.	46	n.d.
Surface tension [mN/m]	1.41	n.d.	n.d.	1.10	1.25 (blatky)	n.d.	n.d.	n.d.	n.d.
Optical Density (OD) on Kompass Copy Office paper	+	-**	-**	+	+	n.d.	n.d.	-**	n.d.
Proof copy after 5 min interval	+	-**	-**	-**	+	n.d.	n.d.	-**	n.d.
Proof copy after 10 min interval	+	-**	-**	-**	+	n.d.	n.d.	-**	n.d.
Proof copy after 20 min interval	+	-**	-**	-**	+	n.d.	n.d.	-**	n.d.
Proof copy after 30 min interval	+	-**	-**	-**	+	n.d.	n.d.	-**	n.d.
Proof copy after 60 min interval	+	-**	-**	-**	+	n.d.	n.d.	-**	n.d.
Nozzle Clogging	no	yes	yes	yes	no	n.d.	n.d.	yes	n.d.
Surface drying at printhead	no	yes	yes	yes	no	n.d.	n.d.	yes	n.d.
Proof copy after 1 d interval	+	-	-	-	+	n.d.	n.d.	-	n.d.
Proof copy after 7 d interval	+	-	-	-	+	n.d.	n.d.	-	n.d.
Overall assessment of printed image	+	-	-	-	0	n.d.	n.d.	-	n.d.

0 = adequate

+ = good

- = poor

** transfer problems

Determining the pH:

The pH is determined from the undiluted suspension.

The following printing tests are performed:

- a. Printing one page onto copier paper and onto various commercial ink jet papers to determine the optical density and for visual assessment of the print quality.
- b. Printing one page after printing intervals of 5, 10, 20, 30 and 60 minutes to assess the transfer and surface drying behavior of the ink.
- c. Refire tests after a printing interval of 1 and 7 days.

The ink according to the invention is characterized by very good printability, high optical densities, and very good storage stability. The inks based on reference sample 6, 7 and 8 resulted in poor long term print results after different print intervals because of nozzle clogging and surface drying on the printhead. Reference sample 9 showed poor optical density and a blotchy print image.

Details of my C.V. are attached hereto.

I, Gerd Tauber, hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so

App. No. 10/627,501
Declar. of Gerd Tauber

made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this declaration is directed.

Date: 07-27-2006


Gerd Tauber

CURRICULUM VITAE

Name: Gerd Tauber
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01.06.1989: AT2/Applied Technology, AEROSIL and celluloses
Elema and UNITAB for pharmaceutical application
since 01.01.1999 AT2/Applied Technology, pigment blacks for Non Impact
Printing focused on Inkjet Ink Dispersions;
Position: Head of R&D group non impact printing

Wolfgang , July 25th, 2006